

## Supporting Information

### Confined space synthesis of fully alloyed AuPd nanoparticles

#### encapsulated in porous silica

*Anupam Samanta, Thattarathody Rajesh and R. Nandini Devi\**

Catalysis and Inorganic Chemistry Division, National Chemical Laboratory, Pune  
411008, India.

### Experimental Section

#### Synthesis of porous-silica encapsulated gold NP

Synthesis of porous-silica encapsulated gold NP has been reported in our previous communications.<sup>1</sup>

#### Synthesis of palladium nanoclusters

Synthesis of palladium nanoclusters has been reported in our previous communications.<sup>2</sup>

#### Synthesis of porous-silica encapsulated palladium NPs

The Pd nanocluster solution (10 mL) was mixed with a 1:4 water/ethanol mixture (200 mL). 0.1M NaOH solution (0.9 mL) and tetraethyl orthosilicate (300  $\mu$ L, Aldrich, 98%) were added to this mixture and stirred at RT for 3 d. Silica-encapsulated palladium nanoclusters were separated from the reaction medium by centrifugation at 14000 rpm and redispersion in water several times. Silica-encapsulated Pd nanoclusters were dried at 100 °C and calcined at 550 °C under air at a ramp of 0.8 min<sup>-1</sup>.

## Details of calculations of CO (mole) conversion per Pd (mole) per second by the four catalysts

### Calculation of CO amount passing through reactor per second

The flow rate of the reaction gas mixture is  $25 \text{ mL min}^{-1}$  (1:5:15.7, CO:O<sub>2</sub>:N<sub>2</sub>).

Amount of CO in 25 mL gas mixture is =1.15 mL.

Temperature of the gas is =  $28 \text{ }^{\circ}\text{C} = 301\text{K}$ .

Volume of CO at STP =  $1.15 \times 273 / 301 = 1.043 \text{ mL}$ .

At STP volume of 1 mole CO is  $22.4 \times 10^3 \text{ mL}$

Then at STP 1.043 mL of CO =  $0.046 \times 10^{-3} \text{ mole CO}$ .

Then amount of CO gas passing through reactor per minute is  $0.046 \times 10^{-3} \text{ mole}$ .

Then amount of CO gas passing through reactor per second  $7.76 \times 10^{-7} \text{ mole}$ .

Then 100 % CO conversion =  $7.76 \times 10^{-7} \text{ mole CO conversion per second}$ .

### Catalyst Au<sub>3</sub>Pd@SiO<sub>2</sub>

Amount of catalyst taken for CO oxidation = 17 mg

Loading of Pd based on ICP-AES = 1.1 %

Amount of Pd in 17 mg catalyst =  $1.757 \times 10^{-6} \text{ mole}$

Temperature (°C)	CO conversion (%)	CO(mole) conversion s <sup>-1</sup>	CO(mole) conversion s <sup>-1</sup> Pd (mole) <sup>-1</sup>
100	0	0	0
180	4	$31.04 \times 10^{-9}$	$1.76 \times 10^{-2}$
190	7	$54.32 \times 10^{-9}$	$3.08 \times 10^{-2}$
200	100	$7.76 \times 10^{-7}$	0.44

### Catalyst AuPd@SiO<sub>2</sub>

Amount of catalyst taken for CO oxidation = 17 mg

Loading of Pd based on ICP-AES = 1.6 %

Amount of Pd in 17 mg catalyst =  $2.55 \times 10^{-6}$  mole

Temperature (°C)	CO conversion (%)	CO(mole) conversion s <sup>-1</sup>	CO(mole) conversion s <sup>-1</sup> Pd (mole) <sup>-1</sup>
100	0	0	0
120	9	$69.84 \times 10^{-9}$	$2.74 \times 10^{-2}$
135	50	$3.88 \times 10^{-7}$	$15.2 \times 10^{-2}$
140	100	$7.76 \times 10^{-7}$	0.30

### Catalyst AuPd<sub>10</sub>@SiO<sub>2</sub>

Amount of catalyst taken for CO oxidation = 17 mg

Loading of Pd based on ICP-AES = 2.48 %

Amount of Pd in 17 mg catalyst =  $3.956 \times 10^{-6}$  mole

Temperature (°C)	CO conversion (%)	CO(mole) conversion s <sup>-1</sup>	CO(mole) conversion s <sup>-1</sup> Pd (mole) <sup>-1</sup>
100	0	0	0
150	5	$38.8 \times 10^{-9}$	$9.80 \times 10^{-3}$
160	19	$147.44 \times 10^{-9}$	$37.26 \times 10^{-3}$
170	100	$7.76 \times 10^{-7}$	0.19

### Catalyst Pd@SiO<sub>2</sub>

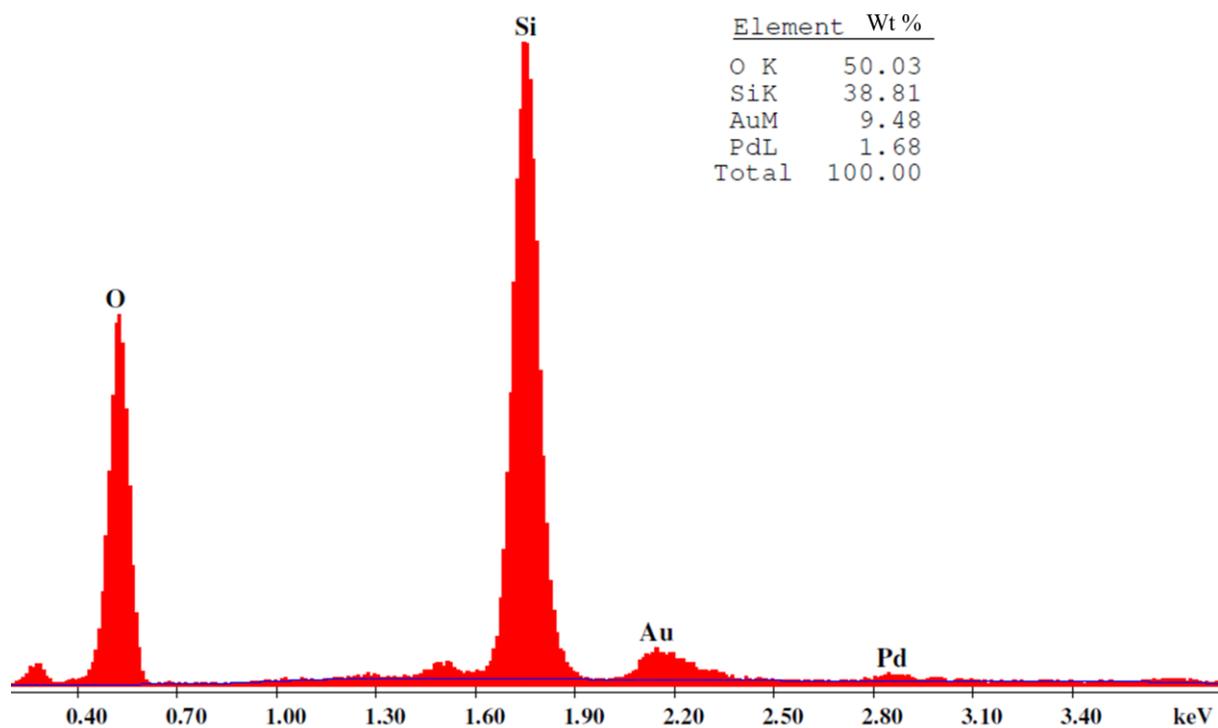
Amount of catalyst taken for CO oxidation = 17 mg

Loading of Pd based on ICP-AES = 2.62 %

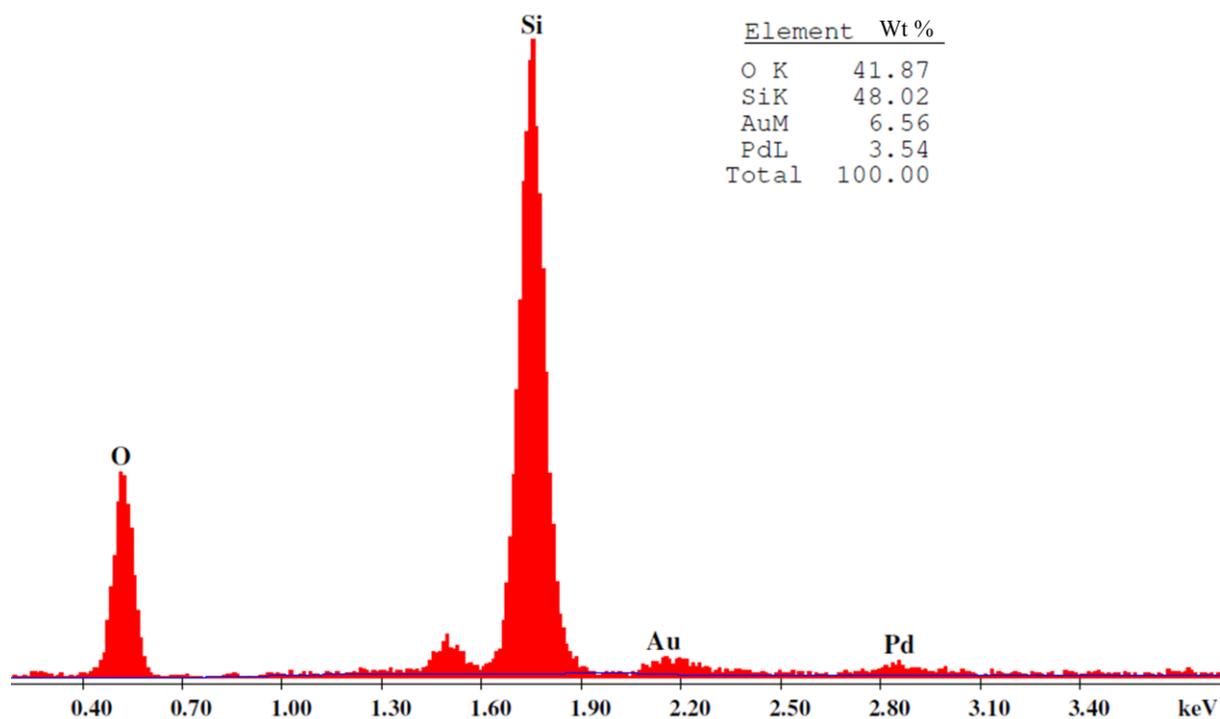
Amount of Pd in 17 mg catalyst =  $4.18 \times 10^{-6}$  mole

Temperature (°C)	CO conversion (%)	CO(mole) conversion s <sup>-1</sup>	CO(mole) conversion s <sup>-1</sup> Pd (mole) <sup>-1</sup>
100	0	0	0
150	4	$31.04 \times 10^{-9}$	$7.42 \times 10^{-3}$
160	12	$93.12 \times 10^{-9}$	$22.27 \times 10^{-3}$
170	100	$7.76 \times 10^{-7}$	0.185

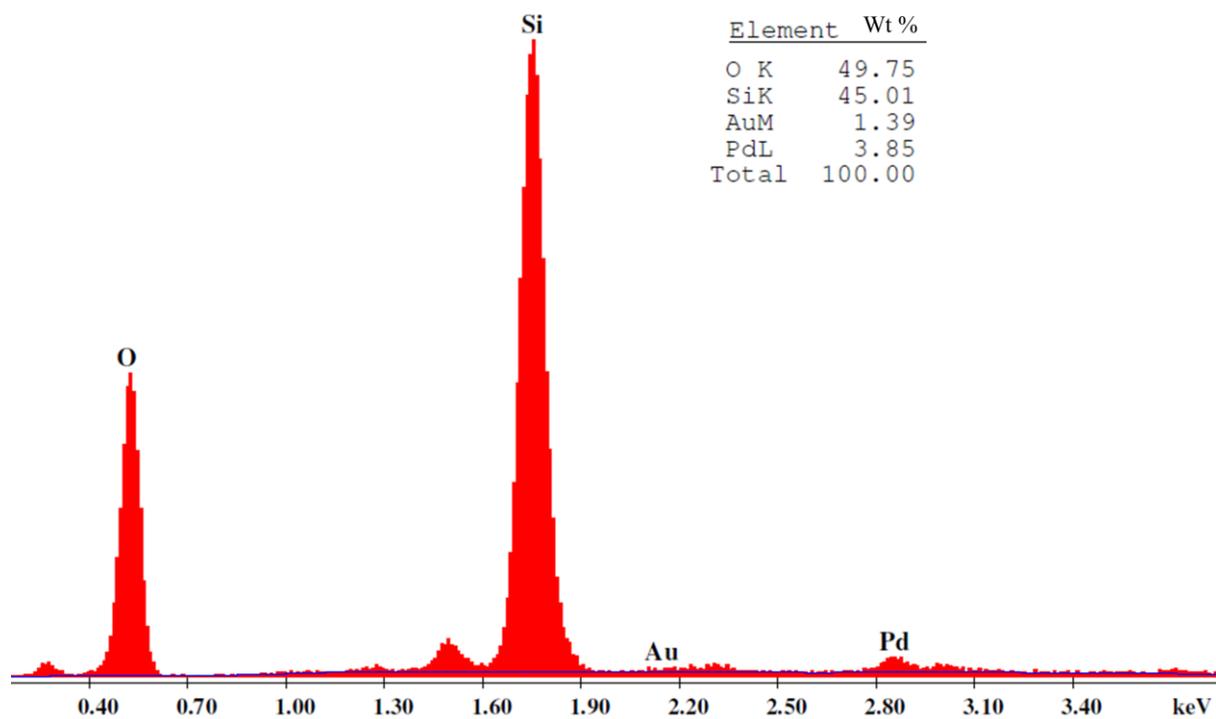
a)



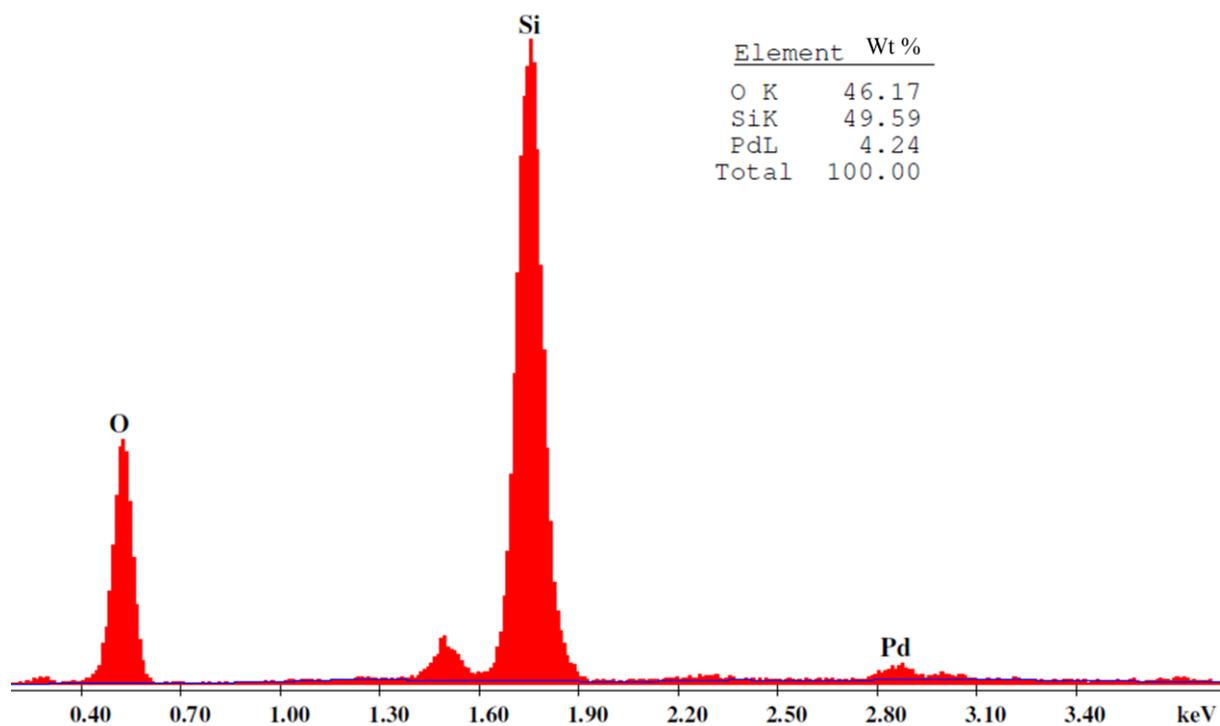
b)



C)

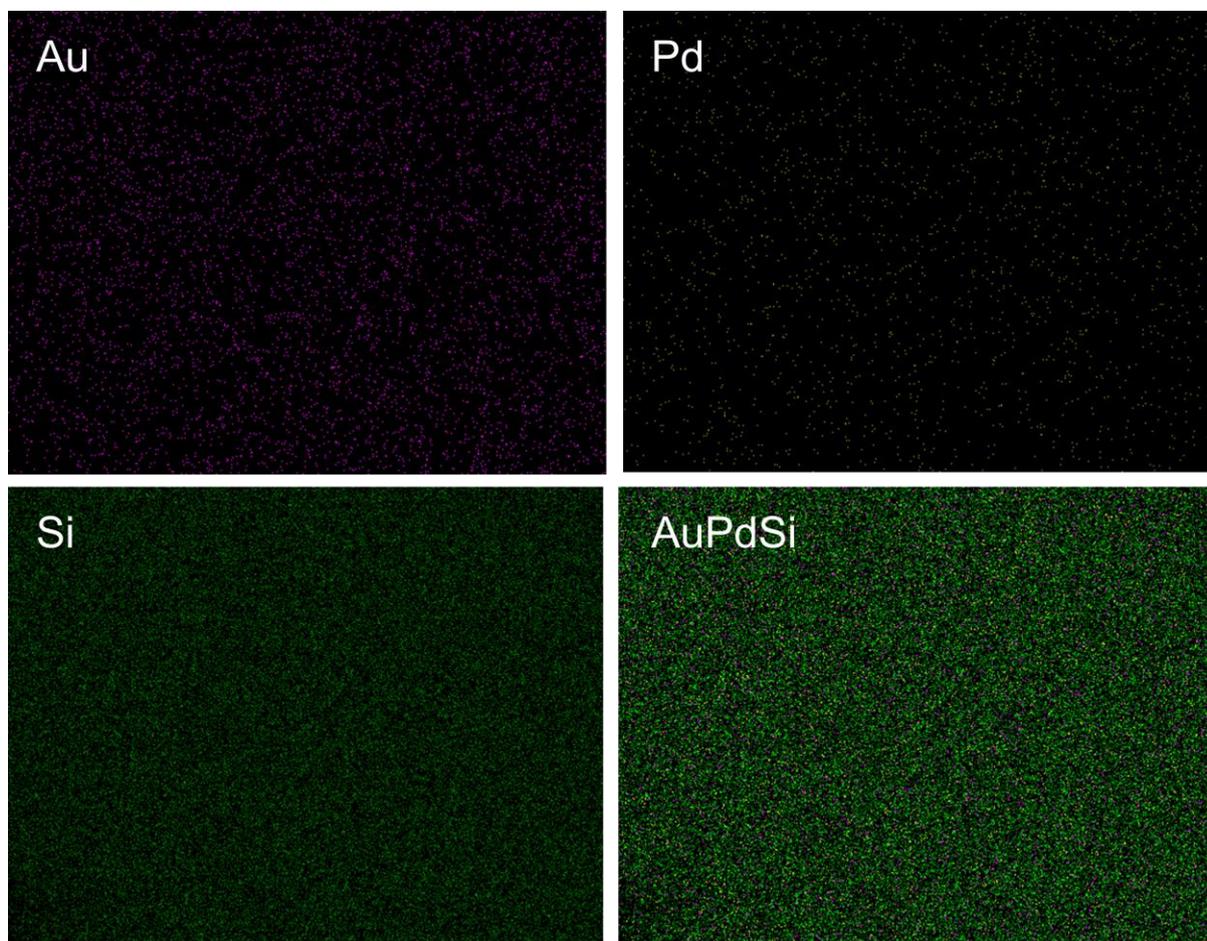


d)

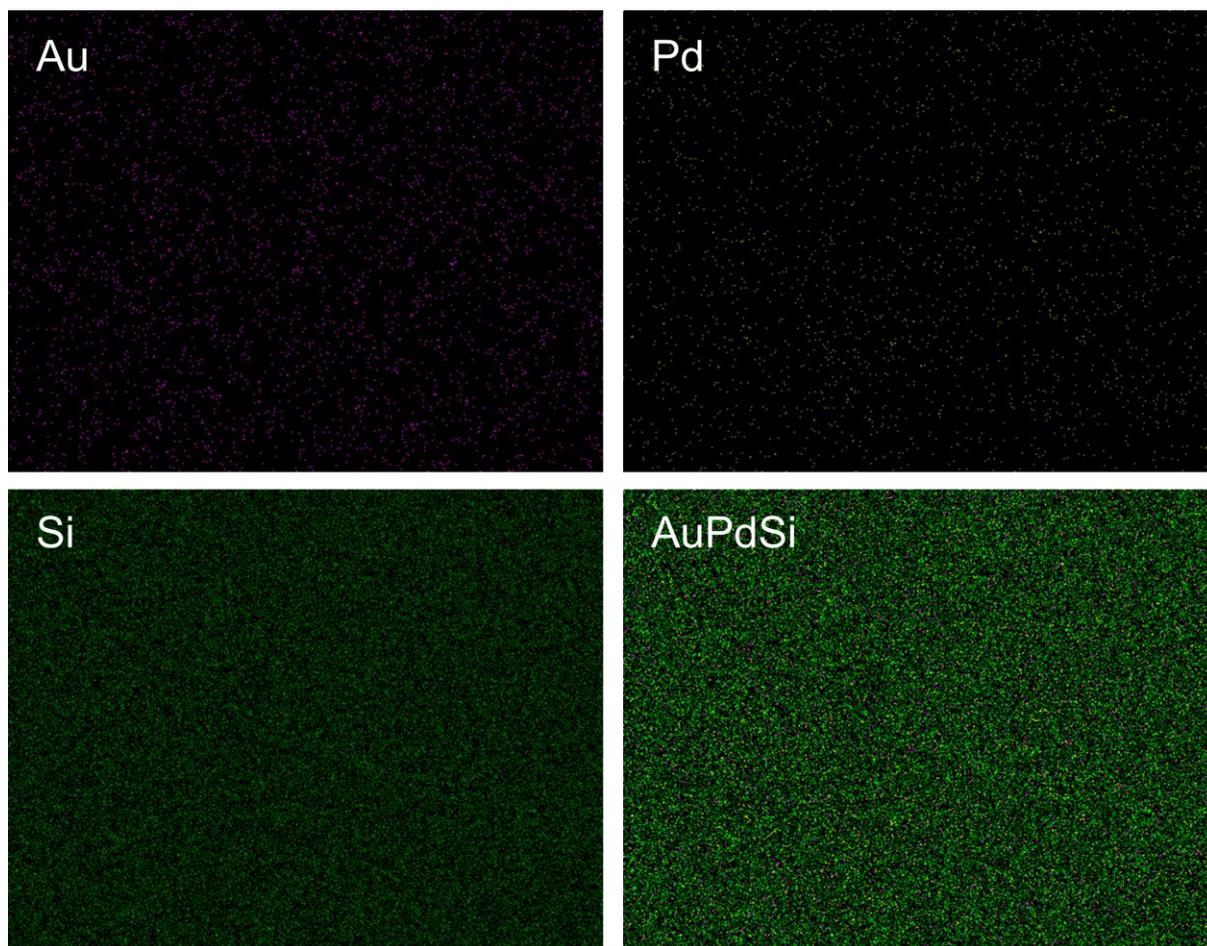


**Supporting Information Figure S1:** EDAX spectra of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub>, c) AuPd<sub>10</sub>@SiO<sub>2</sub>, d) Pd@SiO<sub>2</sub> and respective microanalysis (insets).

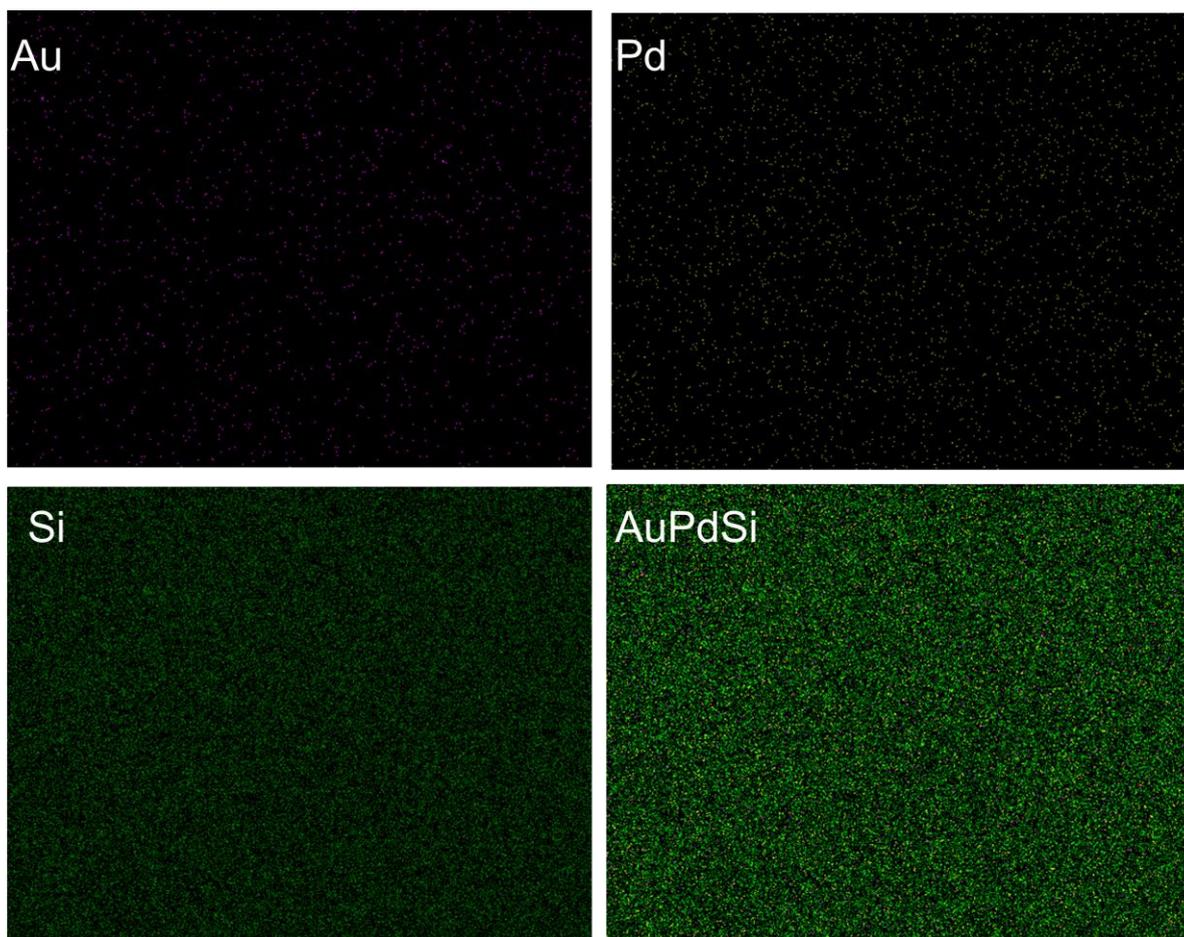
a)



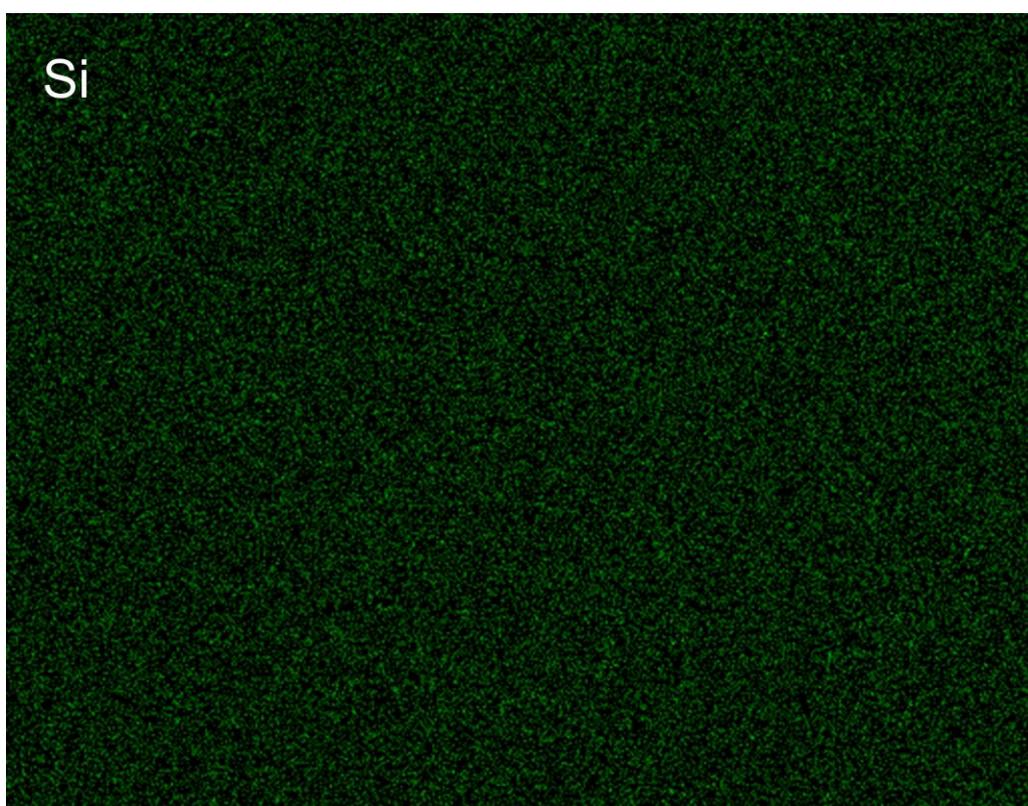
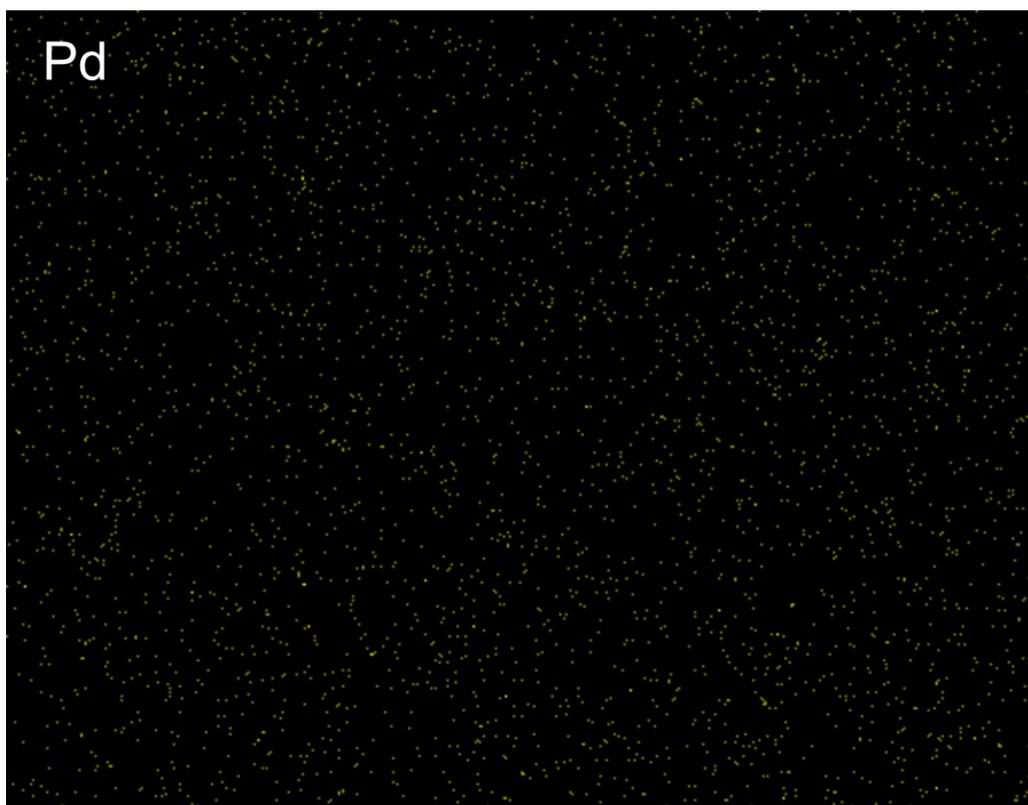
b)

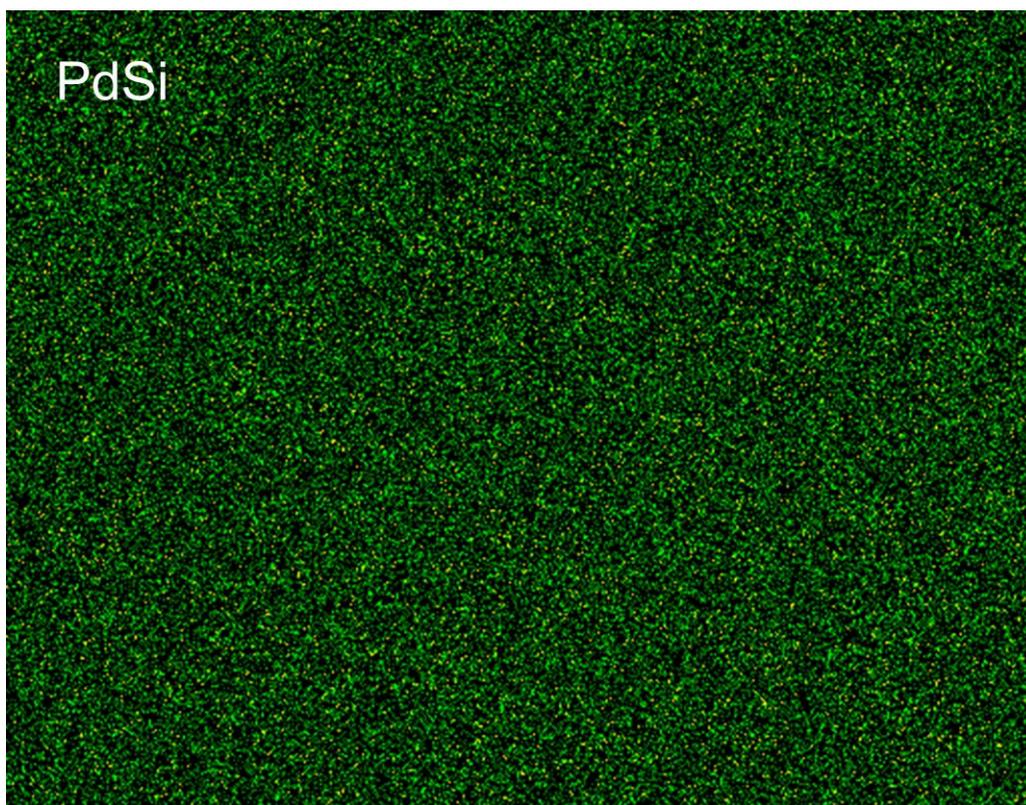


C)



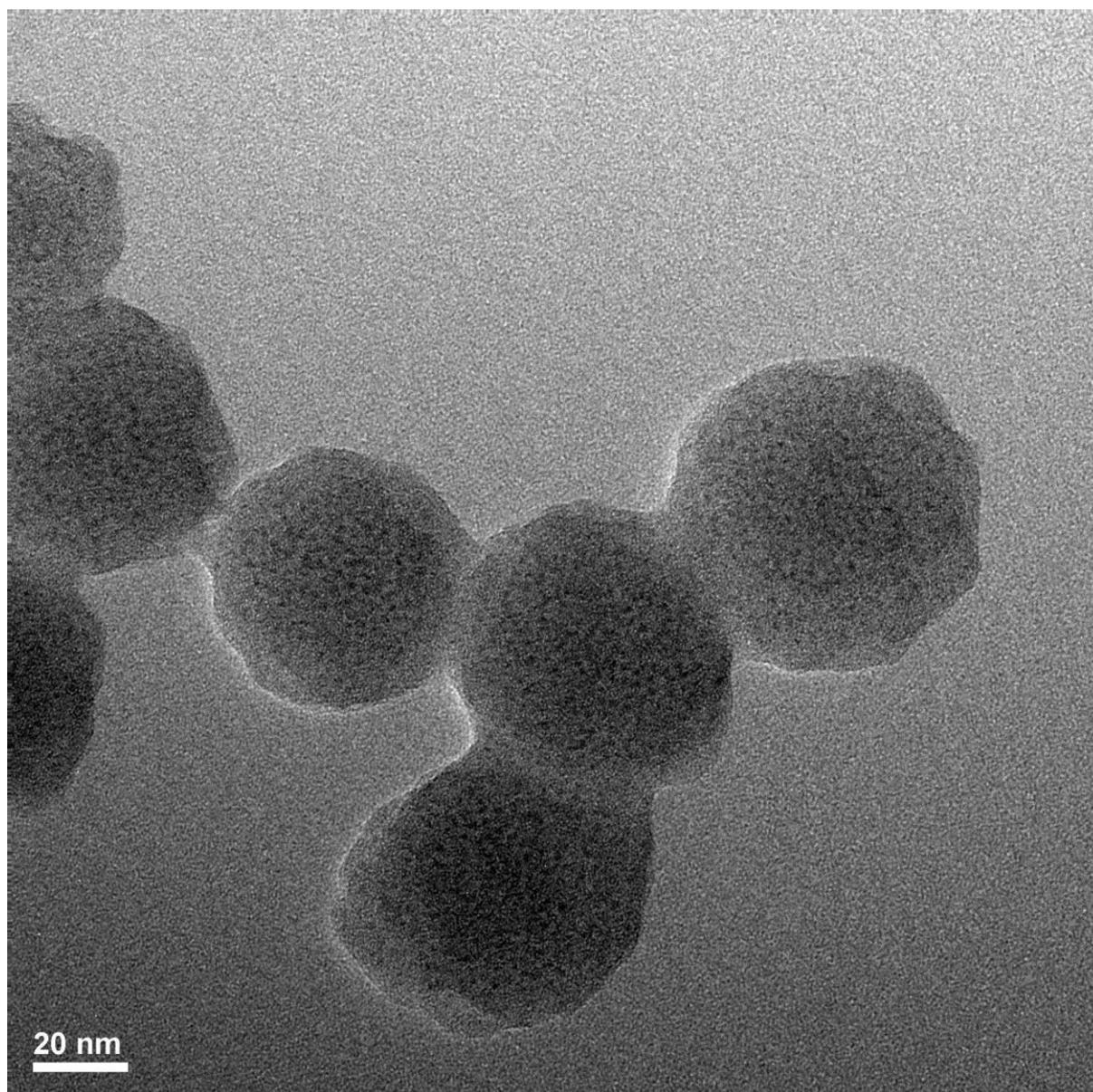
d)



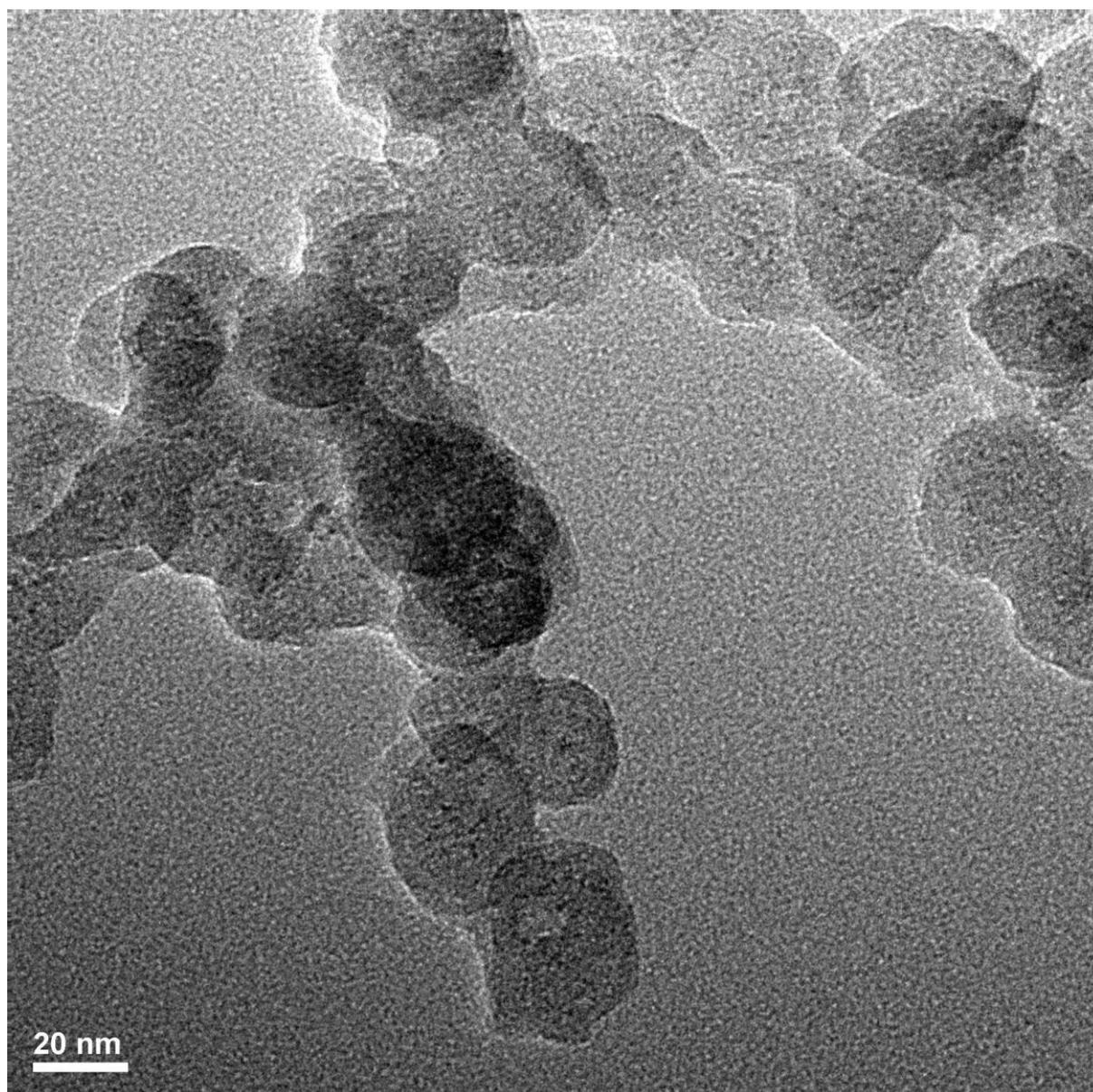


**Supporting Information Figure S2:** SEM elemental mapping analysis of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub>, c) AuPd<sub>10</sub>@SiO<sub>2</sub> and d) Pd@SiO<sub>2</sub>

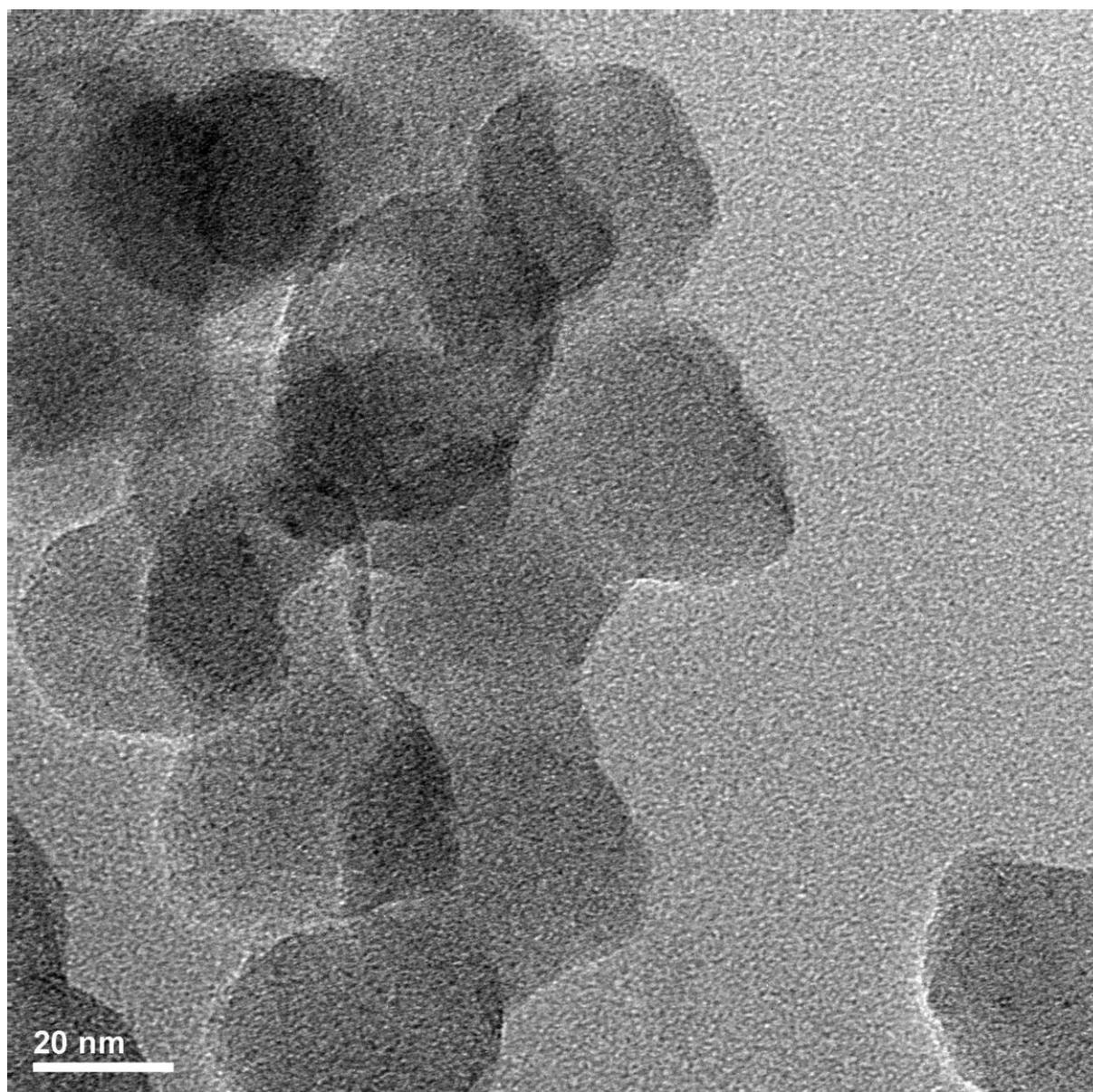
a)



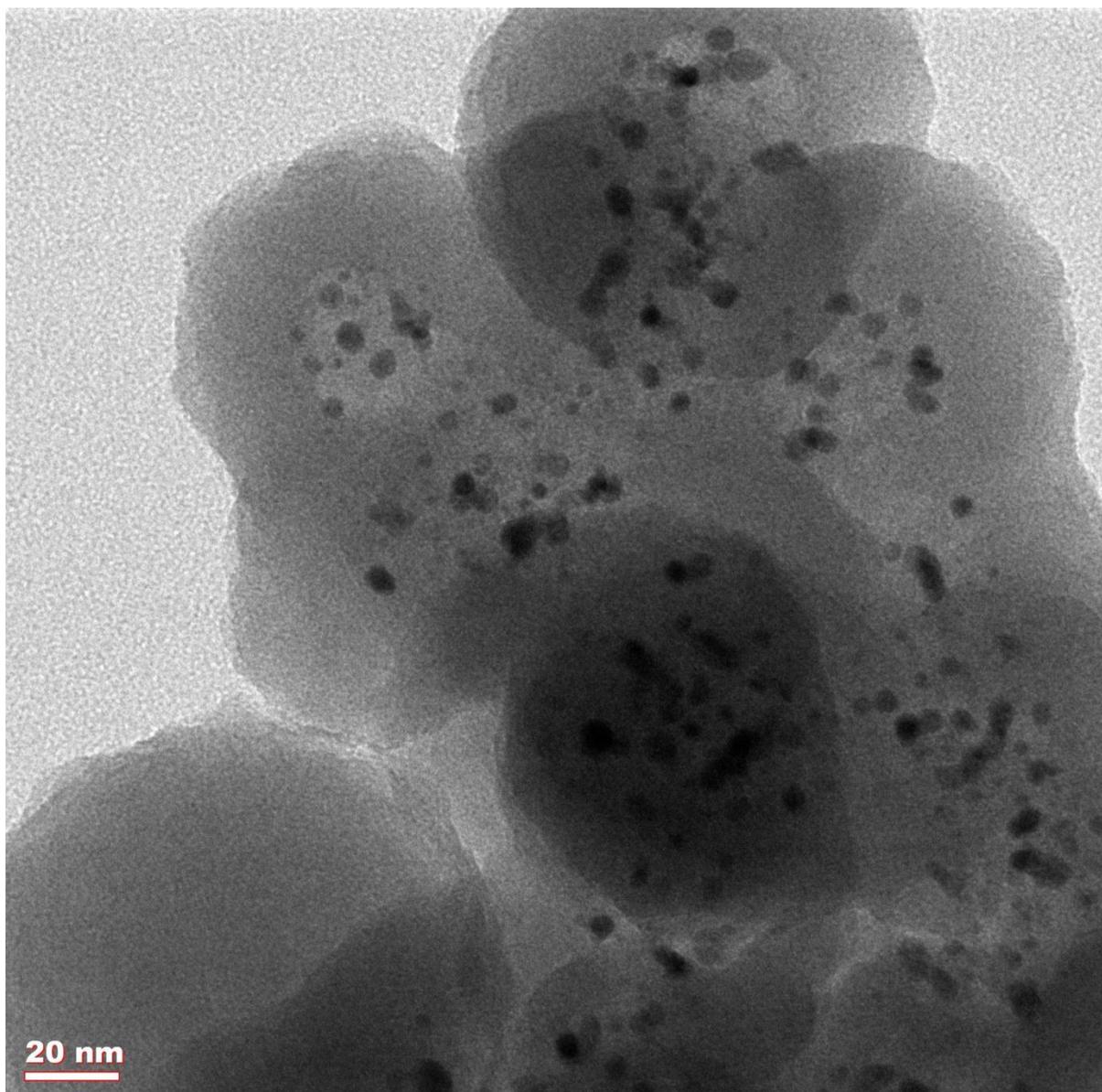
b)



C)

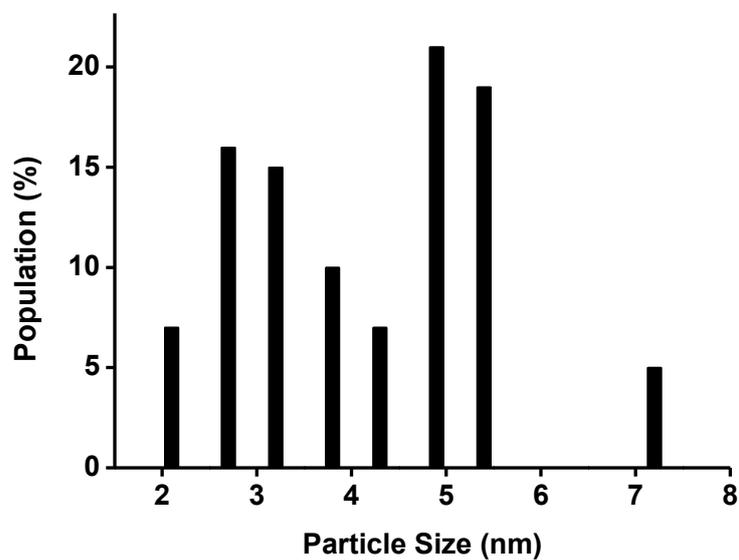


**Supporting Information Figure S3:** HRTEM images of as-synthesized a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub> and C) AuPd<sub>10</sub>@SiO<sub>2</sub>

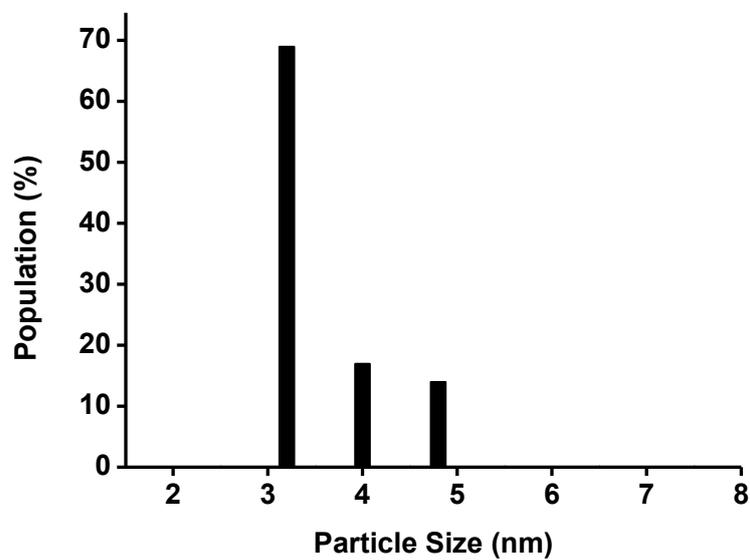


**Supporting Information Figure S4:** TEM image of silica encapsulated gold nanoparticles. A Gatan digital camera (Orius SC 600 A, Gatan, 1024 x 1024 pixels) at 1000 –1000000 x magnification was used to record the micrographs. Sample synthesized by an excess of TEOS. 1 mL of 0.1 M NaOH and 200  $\mu$ L of TEOS were used for 5 mL of Au cluster solution. The product was filtered, dried and calcined at 500  $^{\circ}$ C.

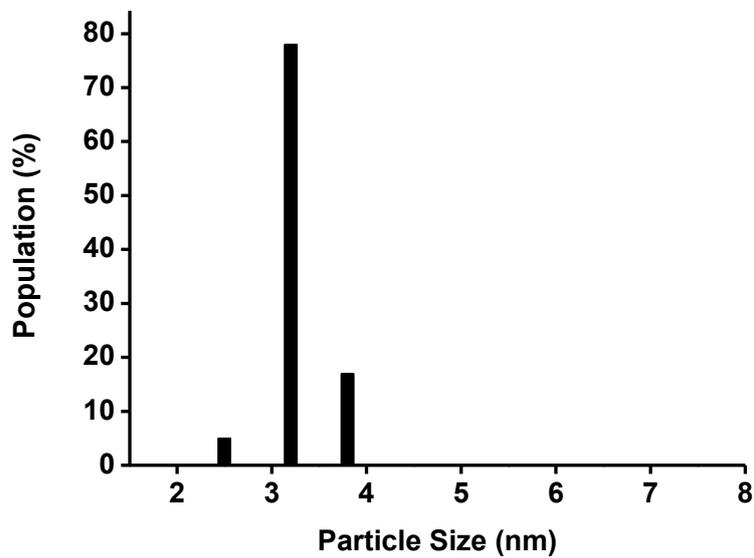
a)



b)

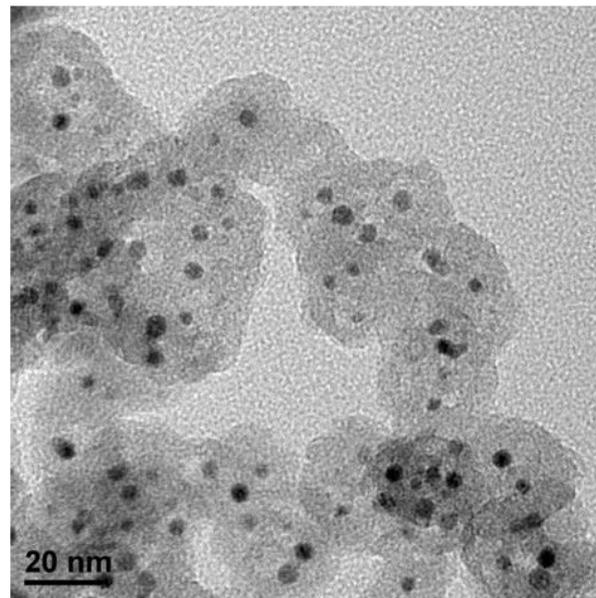
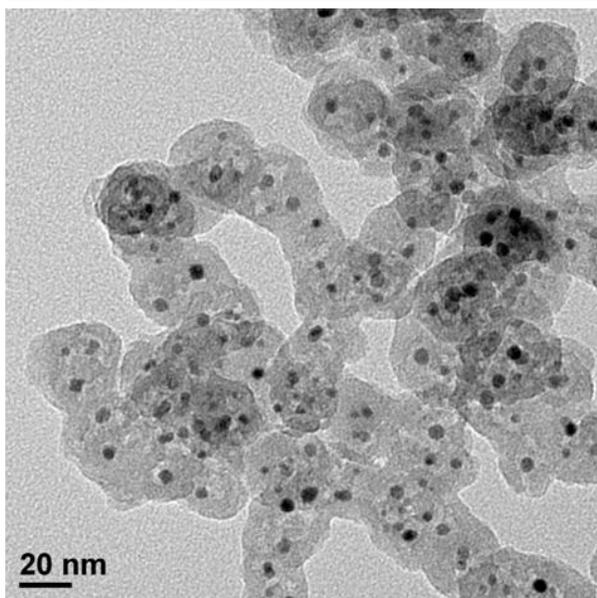
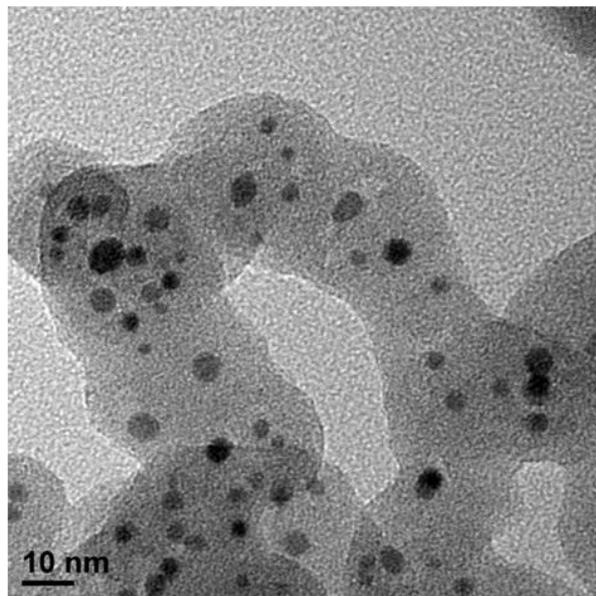
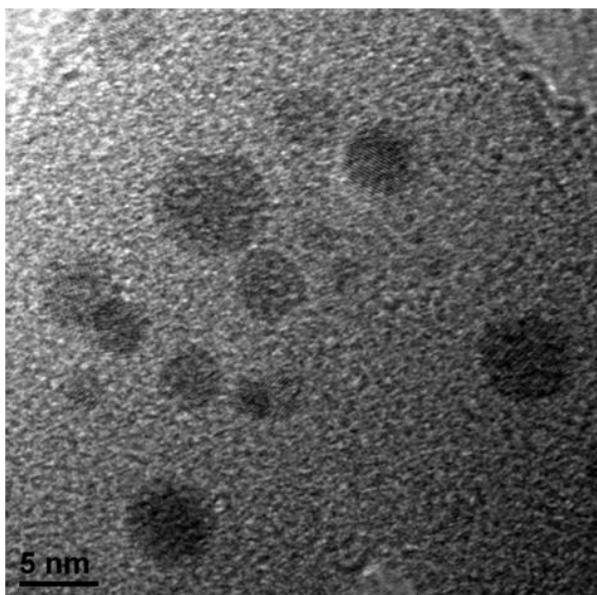


C)

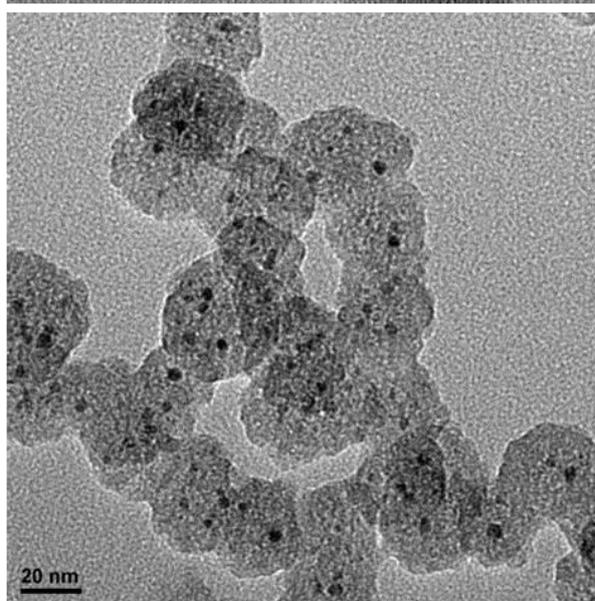
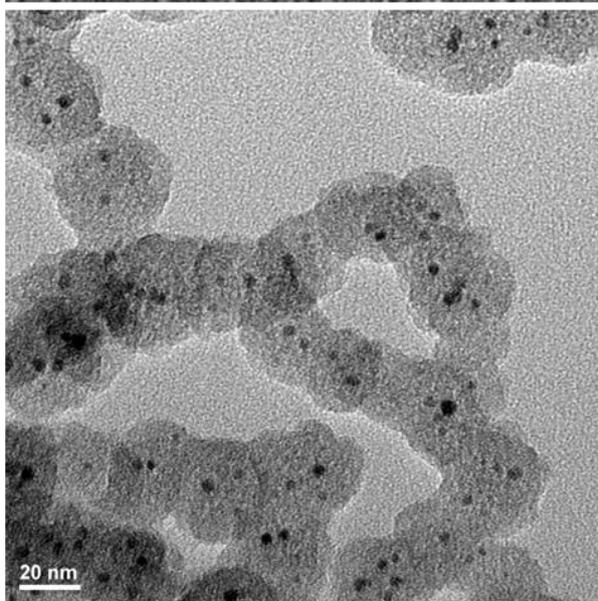
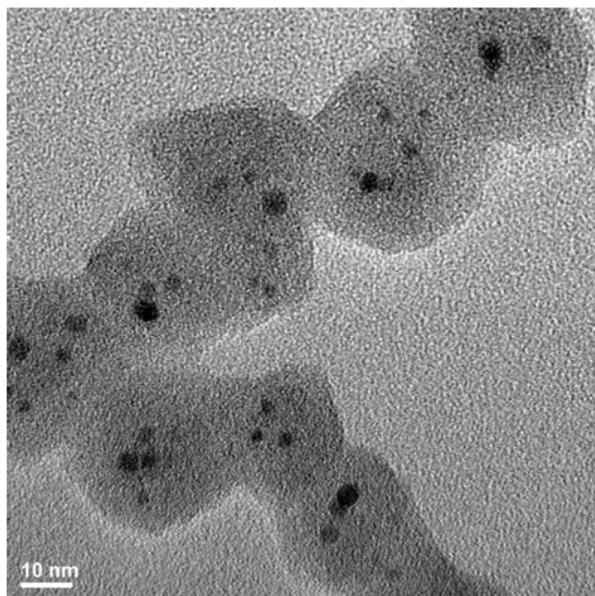
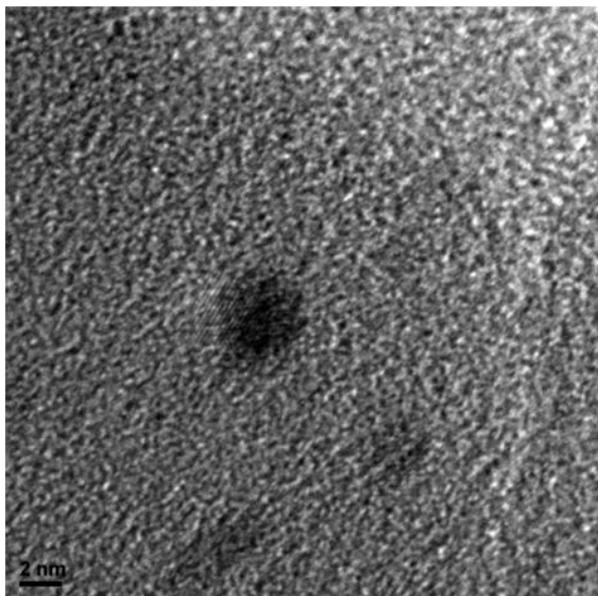


**Supporting Information Figure S5:** Particle size distribution graph of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub> and C) AuPd<sub>10</sub>@SiO<sub>2</sub> calcined at 550 °C.

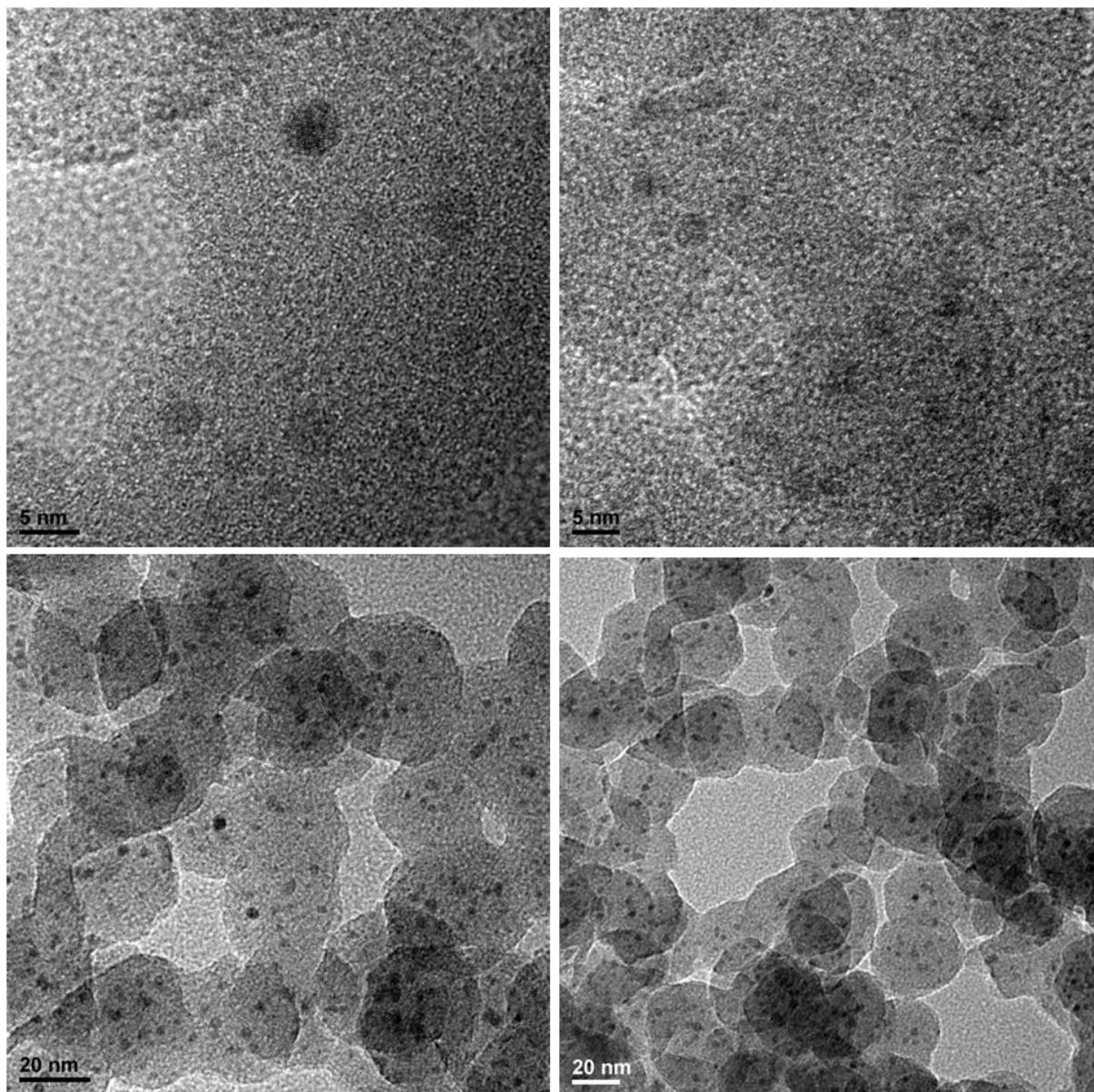
a)



b)

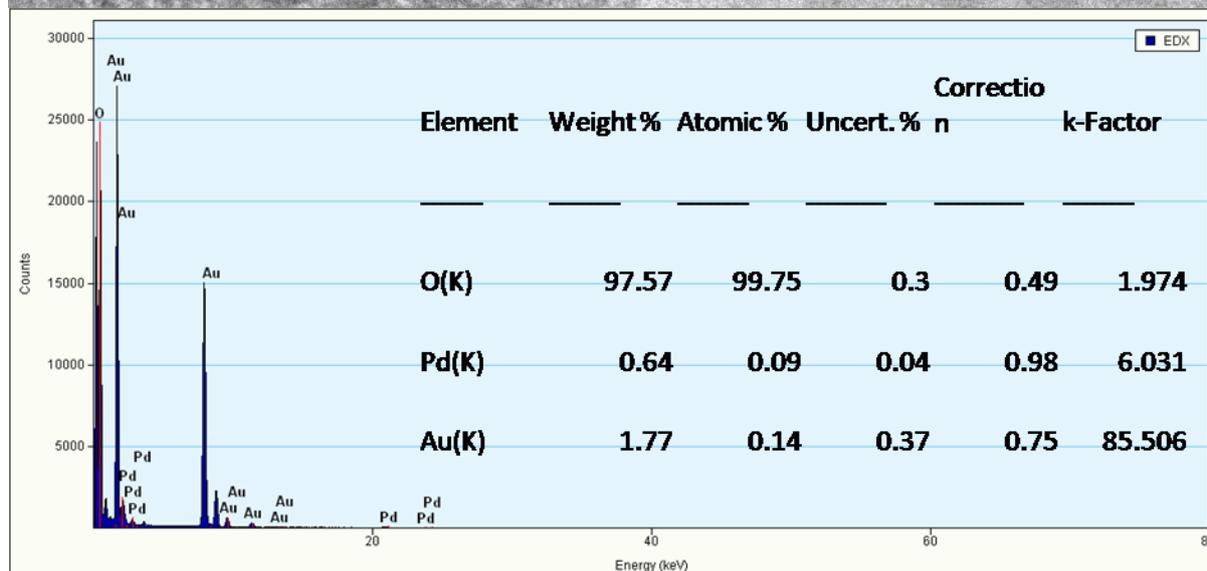
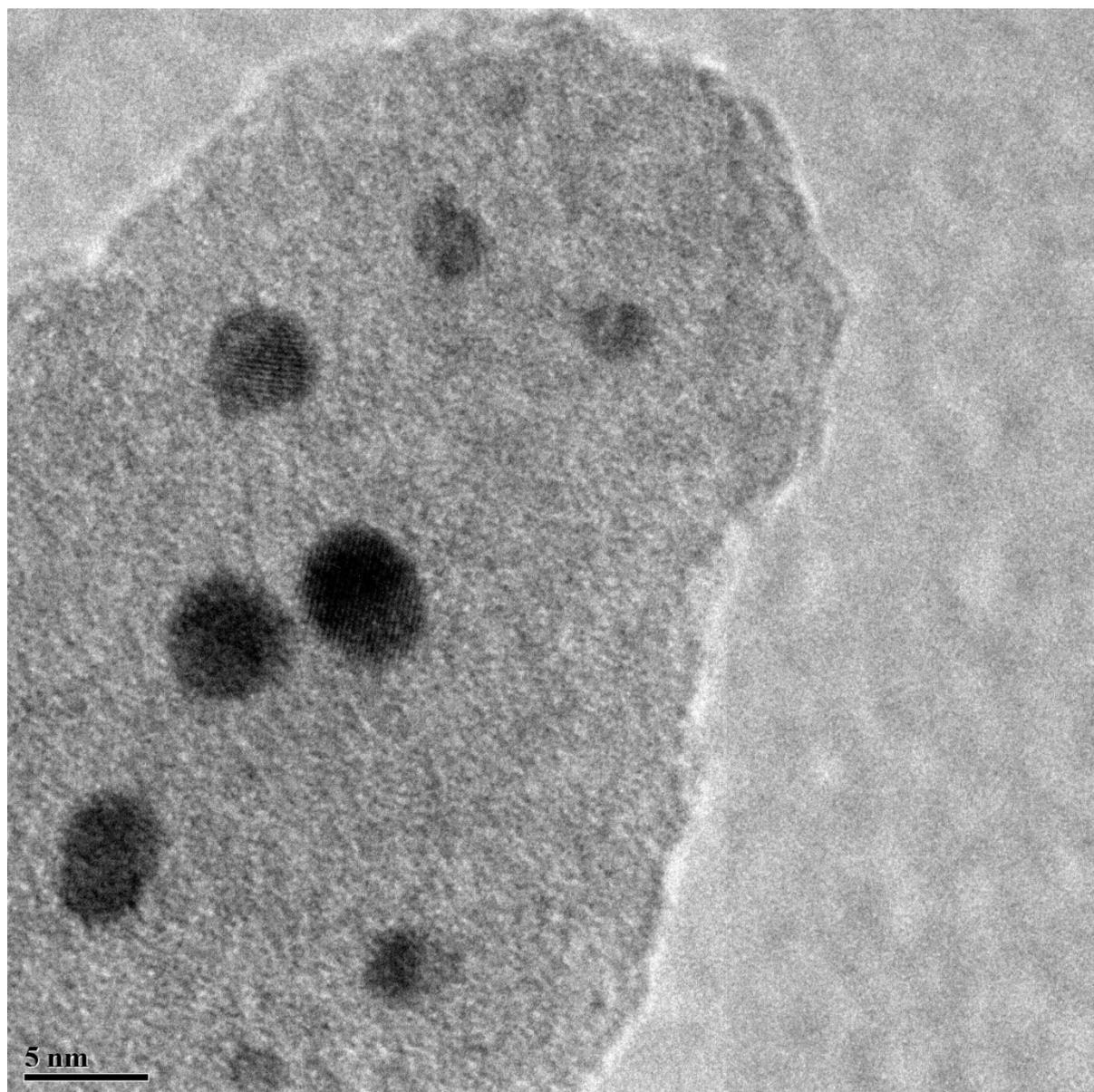


C)

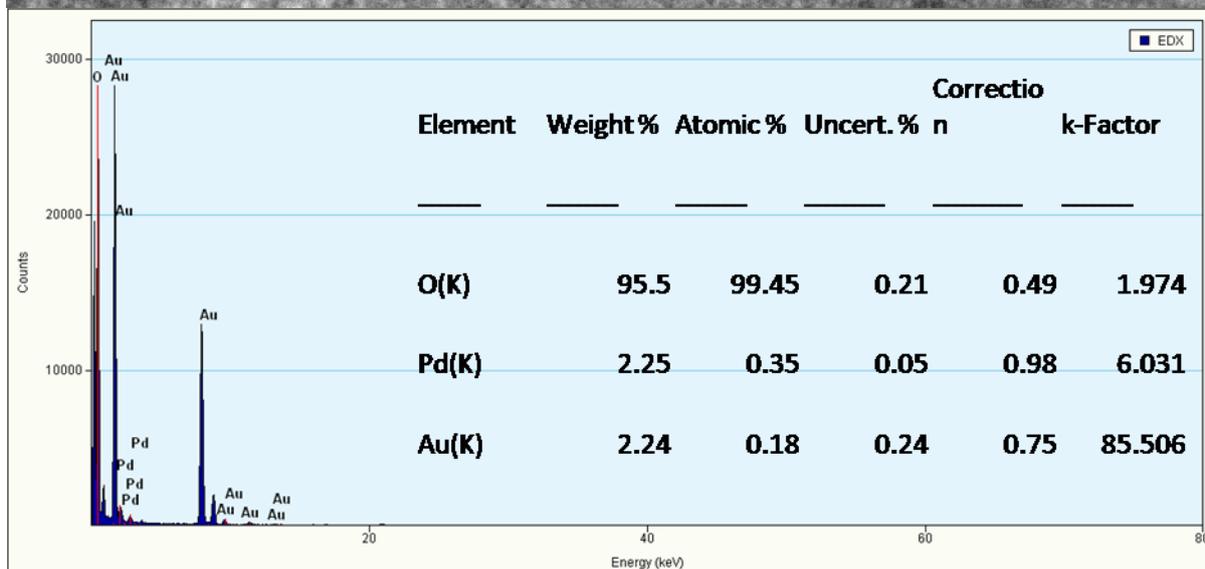
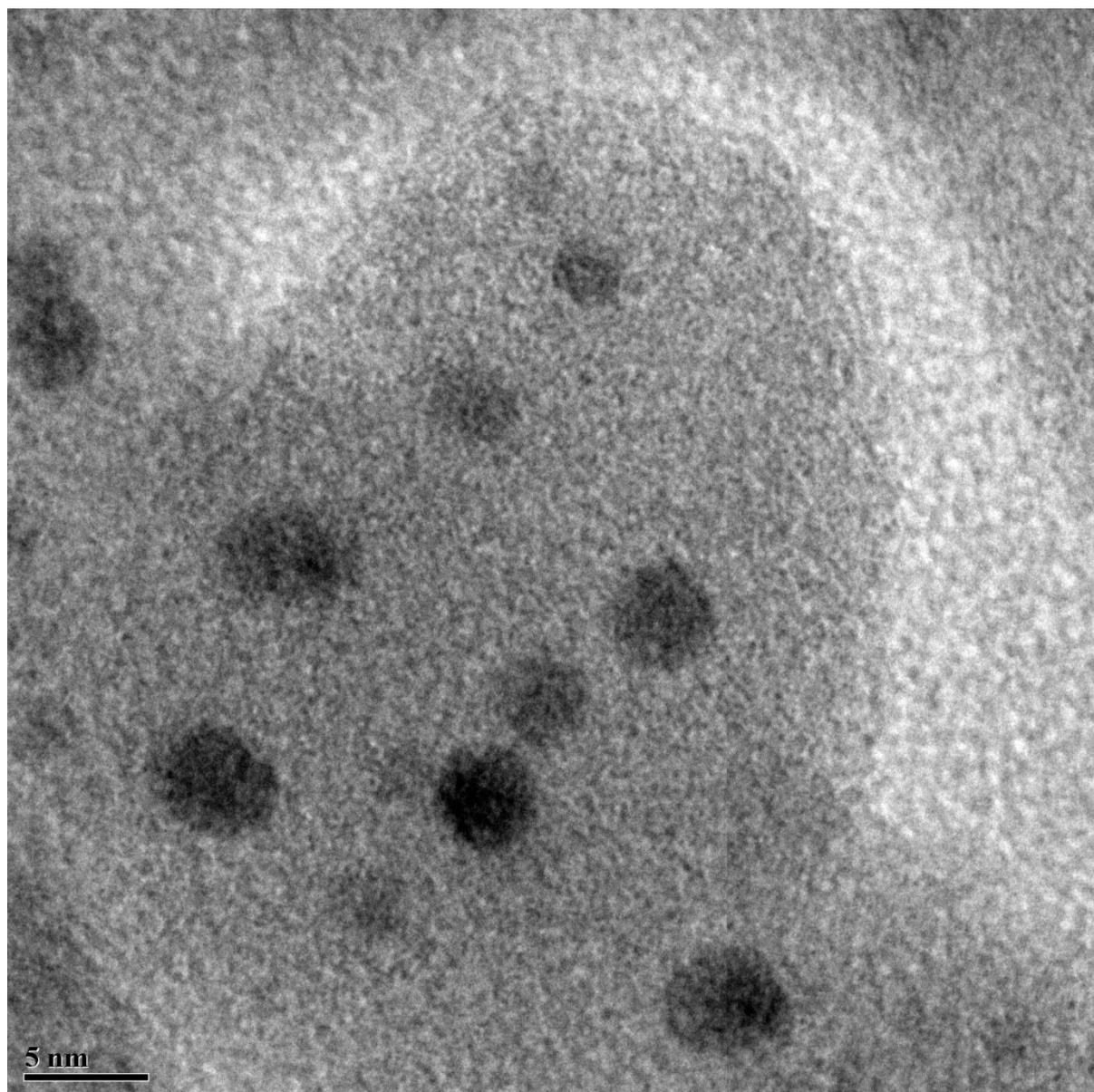


**Supporting Information Figure S6:** HRTEM images of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub>, and C) AuPd<sub>10</sub>, used for determining average particle size distribution. A Gatan digital camera (US 1000, Gatan2048 x 2048 pixels) at 51 – 1000000 x magnification was used to record micrographs.

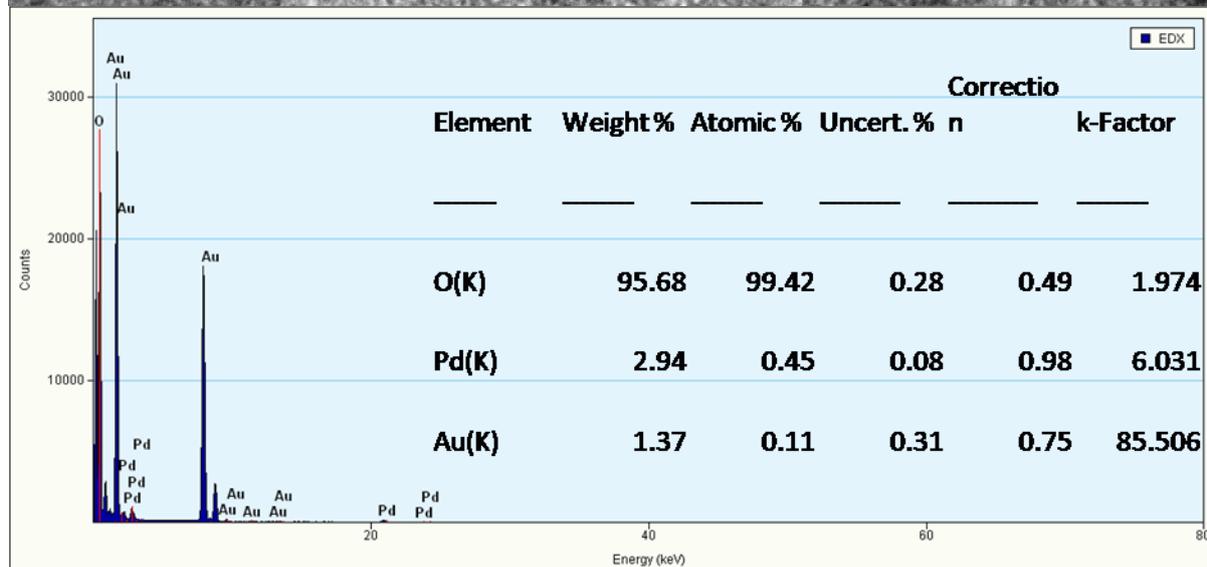
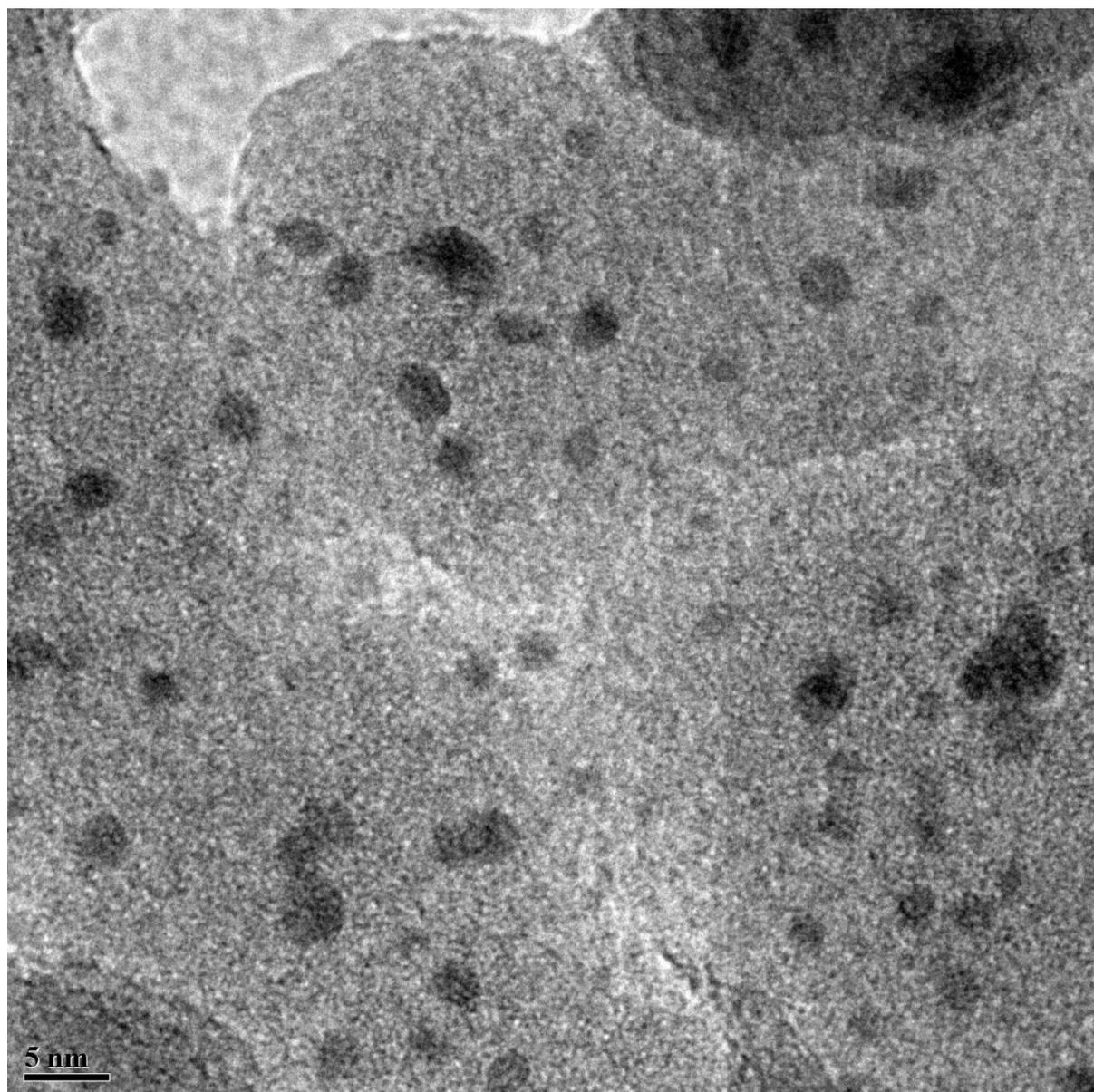
a)



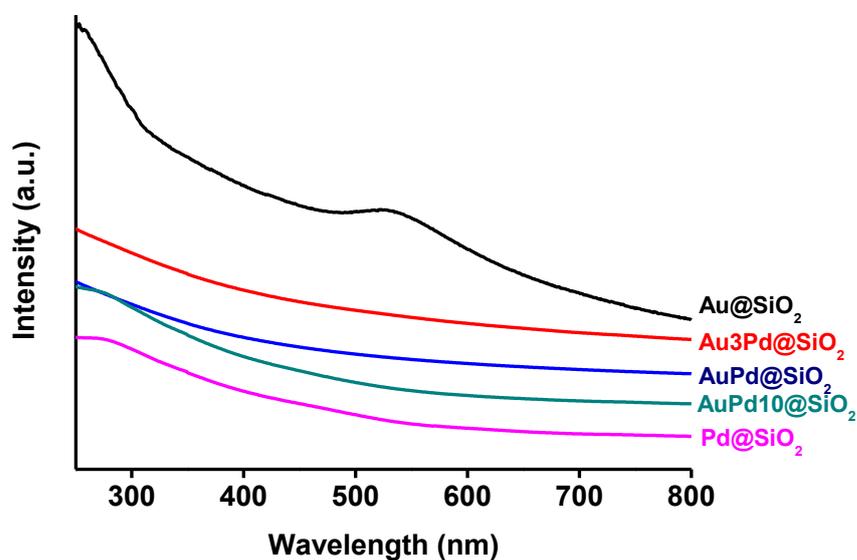
b)



C)

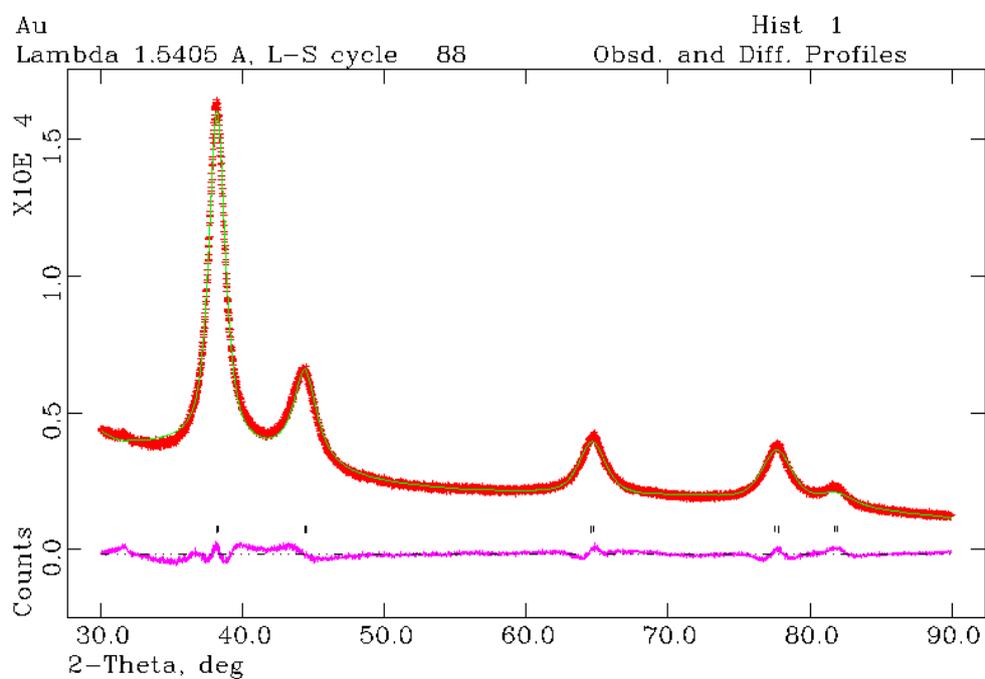


**Supporting Information Figure S7:** Selected area TEM-EDX analysis of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub> and c) AuPd<sub>10</sub>@SiO<sub>2</sub> and respective microanalysis (below).

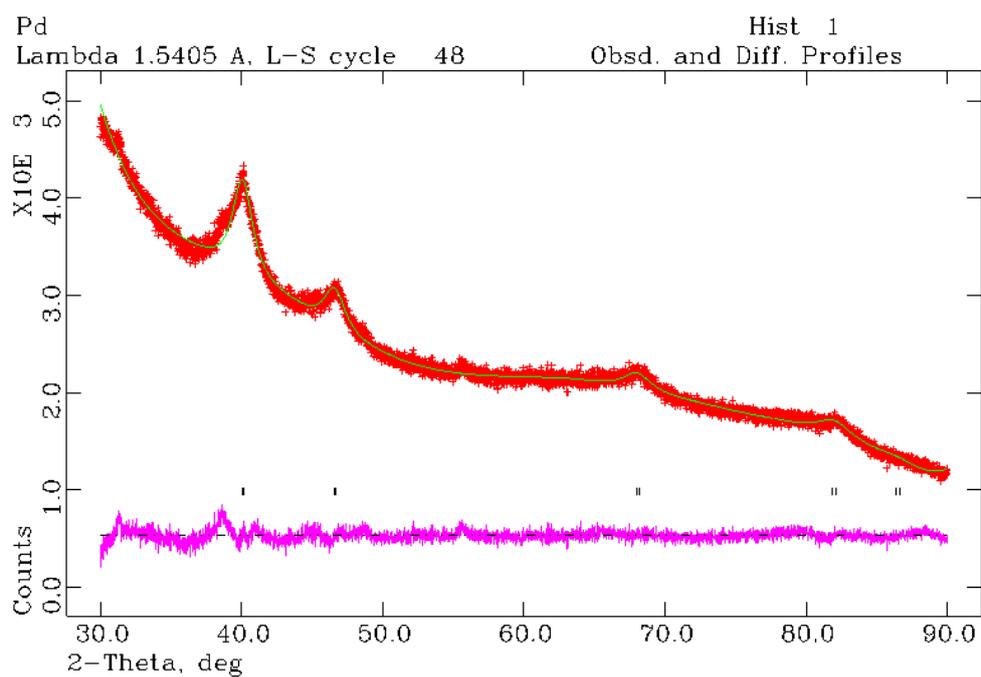


**Supporting Information Figure S8:** UV-visible spectra of Au@SiO<sub>2</sub>, Au<sub>3</sub>Pd@SiO<sub>2</sub>, AuPd@SiO<sub>2</sub>, AuPd<sub>10</sub>@SiO<sub>2</sub> and Pd@SiO<sub>2</sub>.

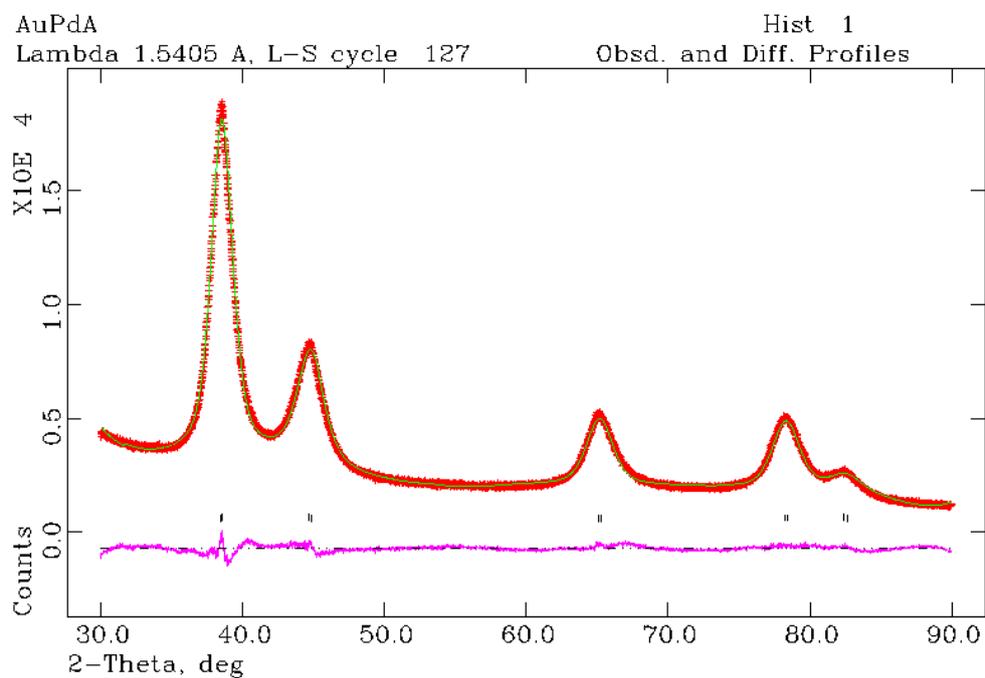
a)



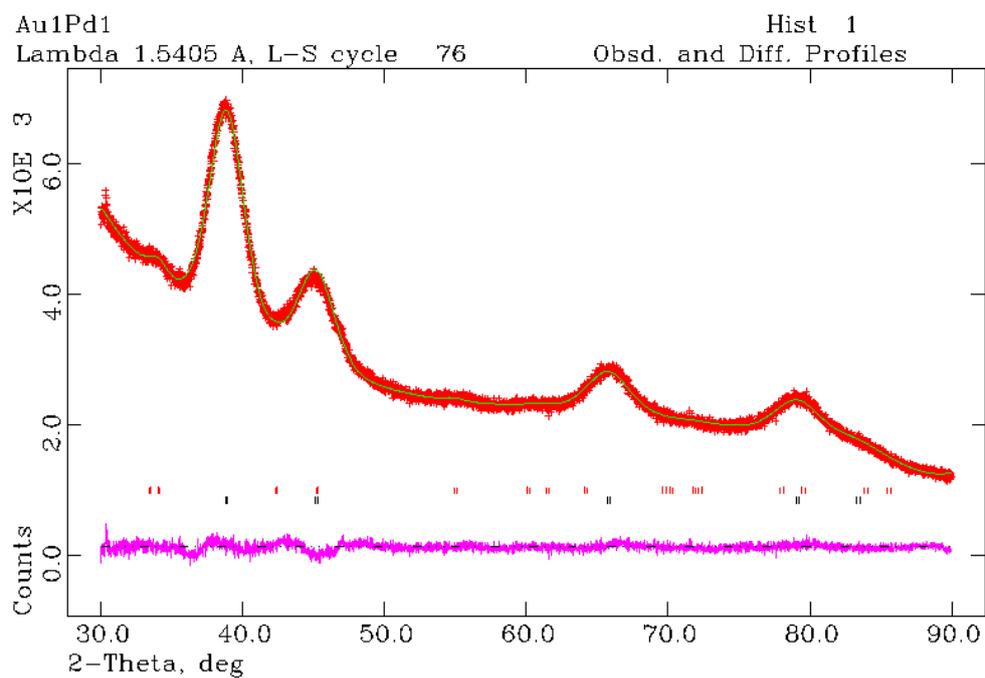
b)



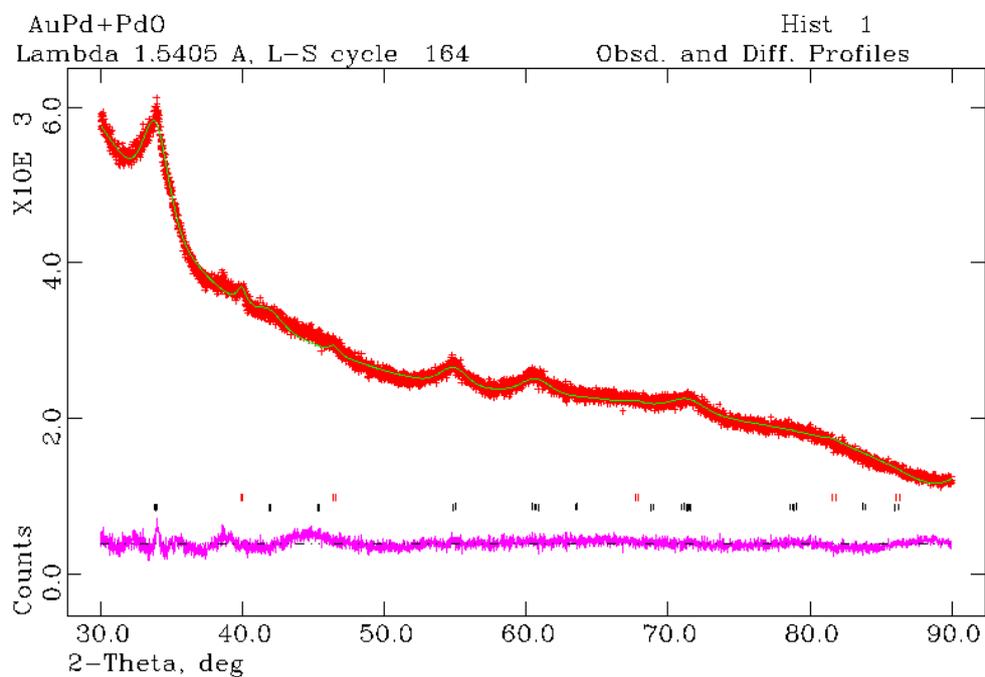
c)



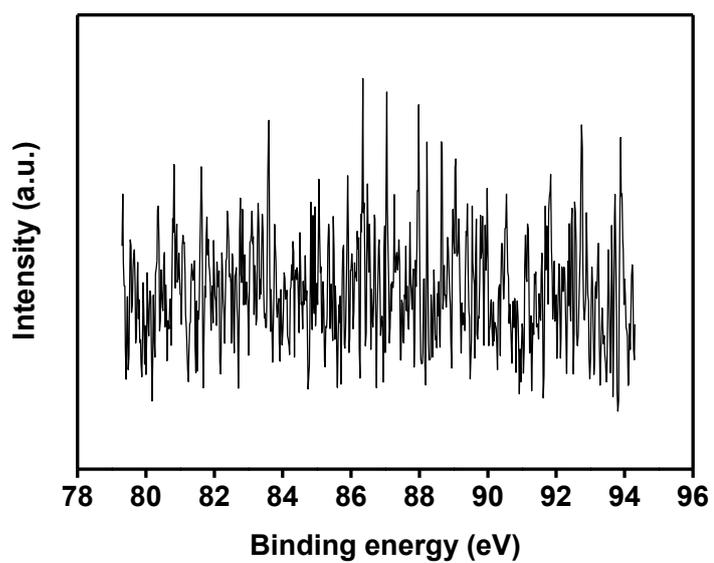
d)



e)

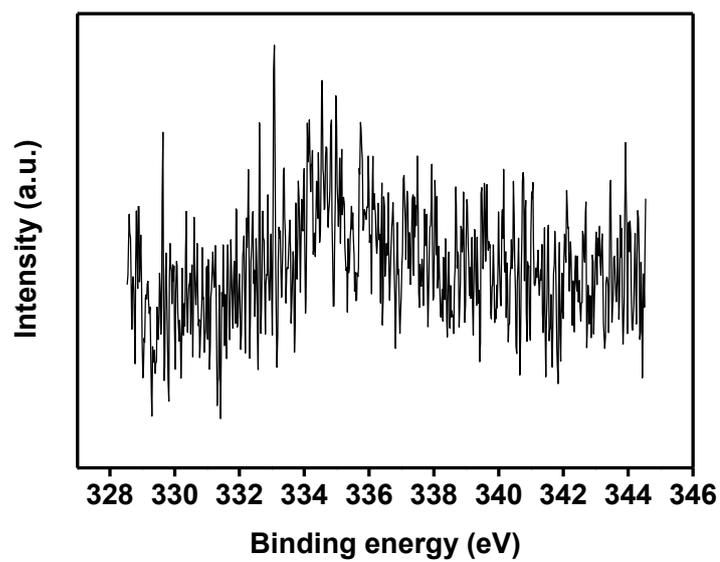


**Supporting Information Figure S9:** Rietveld refinement of a) Au@SiO<sub>2</sub>, b) Pd@SiO<sub>2</sub>, (reduced) c) Au<sub>3</sub>Pd@SiO<sub>2</sub>, d) AuPd@SiO<sub>2</sub>, and e) AuPd<sub>10</sub>@SiO<sub>2</sub>.

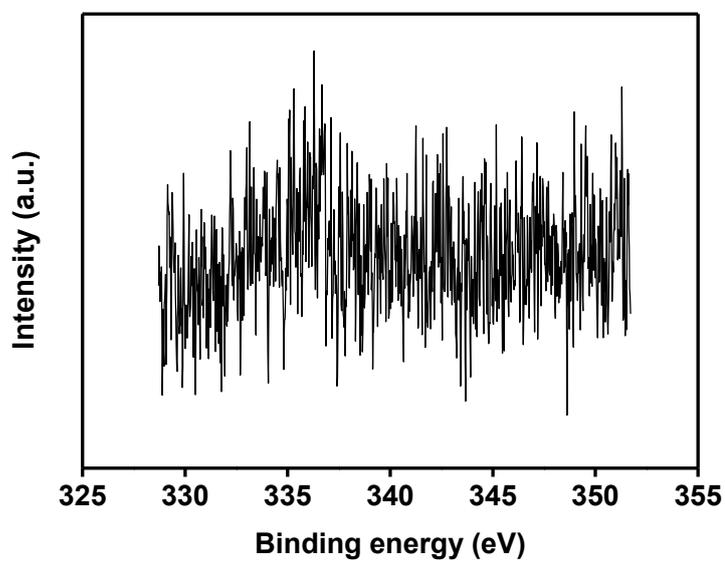


**Supporting Information Figure S10:** Au XPS spectrum of AuPd10@SiO<sub>2</sub>.

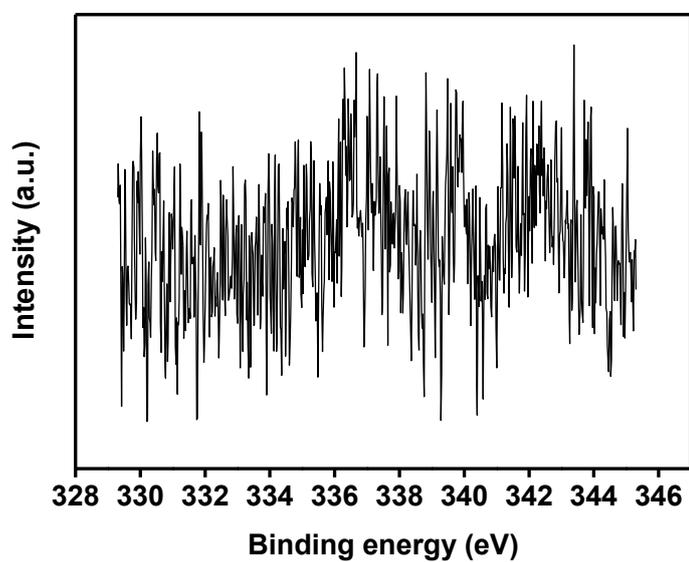
a)



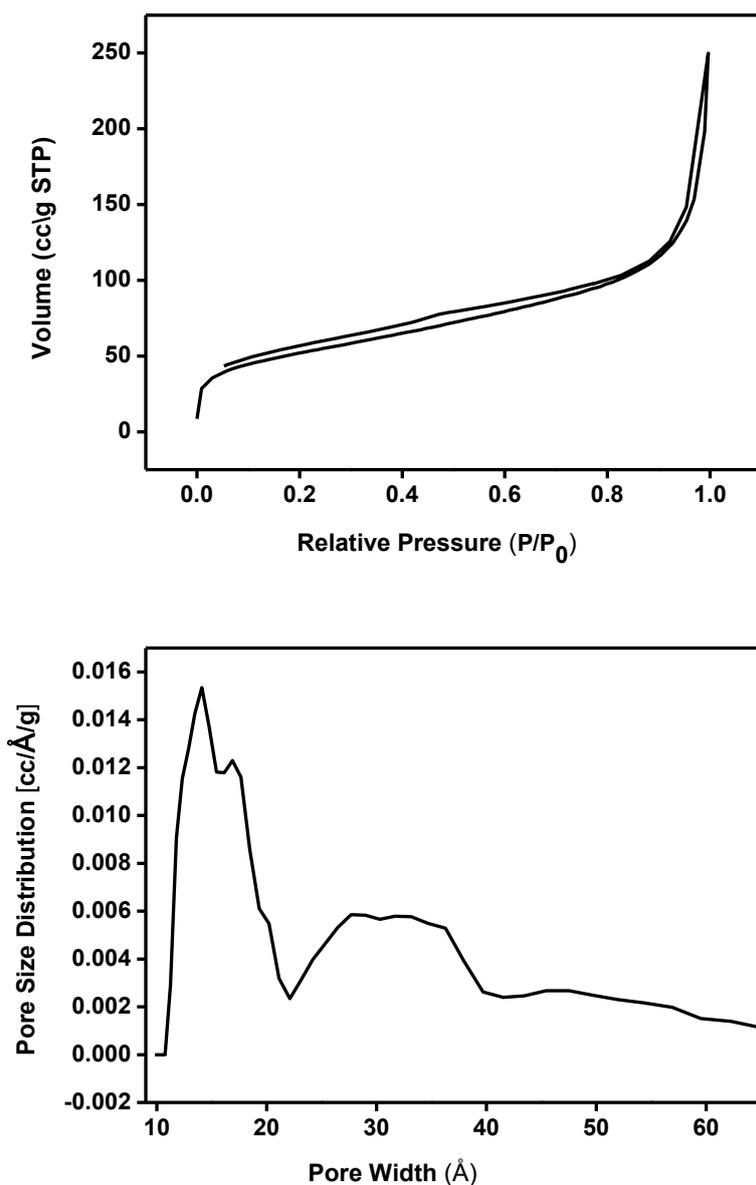
b)



c)



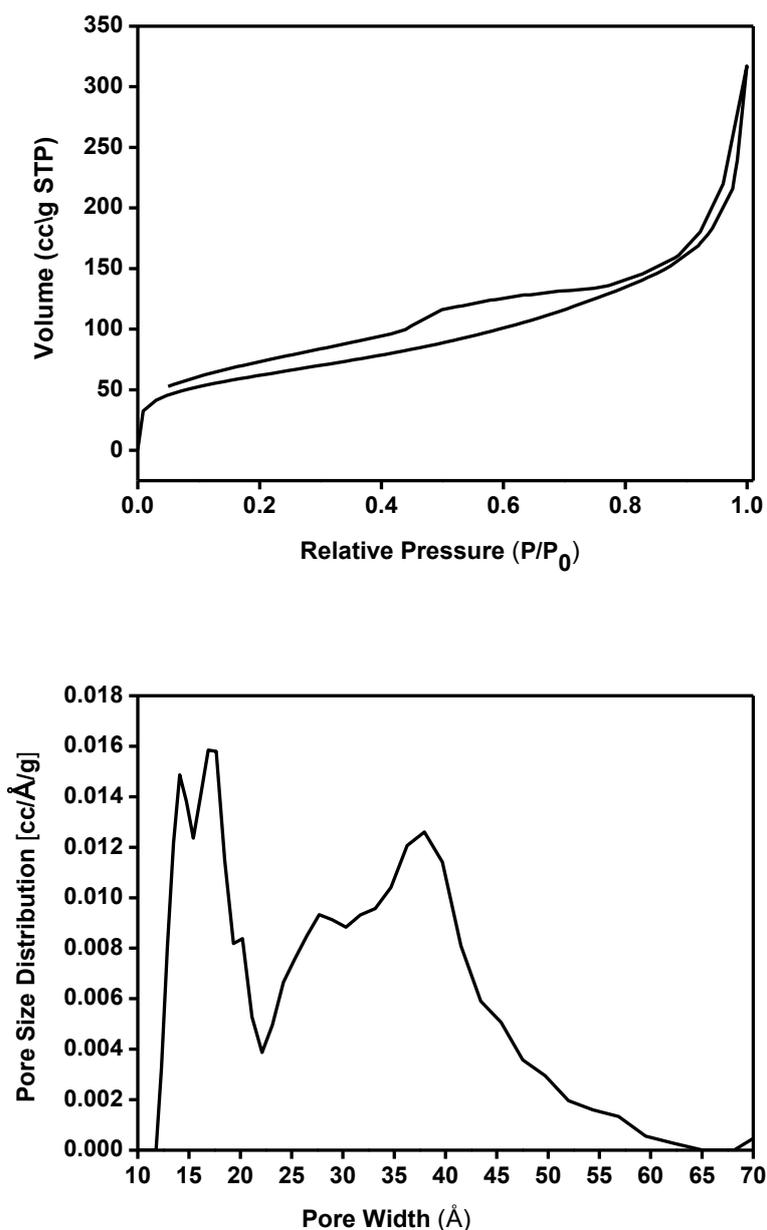
**Supporting Information Figure S11:** Pd XPS spectra of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub> and c) AuPd<sub>10</sub>@SiO<sub>2</sub>.



**Supporting Information Figure S12:** (top) N<sub>2</sub> adsorption – desorption isotherms of sample Au<sub>3</sub>Pd@SiO<sub>2</sub> (bottom) Pore size distribution calculated from the adsorption branch of the isotherms by DFT method.

N <sub>2</sub> uptake (cm <sup>3</sup> g <sup>-1</sup> STP)	250
Total Pore Volume <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	0.38
Micropore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	0.02

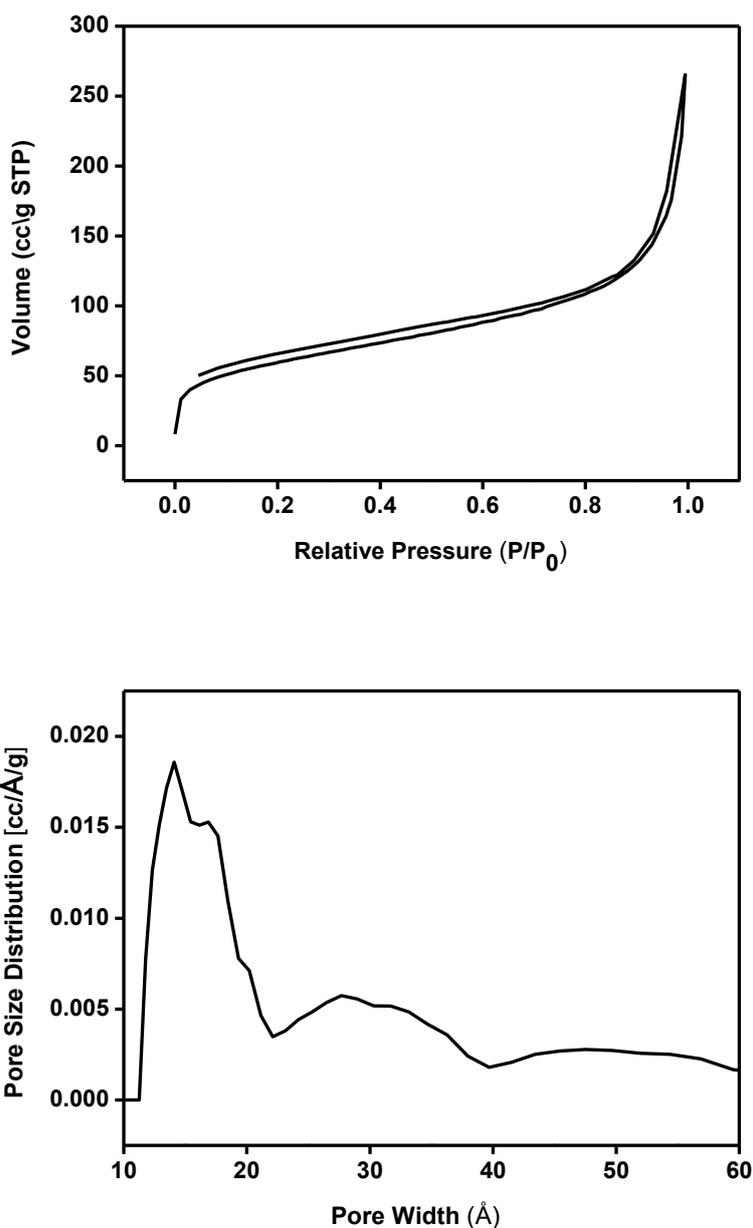
<sup>a</sup>Total pore volume measured at a relative pressure of P/P<sub>0</sub> = 0.99. <sup>b</sup> Calculated through t-plot analysis as a function of relative pressure using the Broekhoff de Boer model.



**Supporting Information Figure S13:** (top) N<sub>2</sub> adsorption – desorption isotherms of sample AuPd@SiO<sub>2</sub> (bottom) Pore size distribution calculated from the adsorption branch of the isotherms by DFT method.

N <sub>2</sub> uptake (cm <sup>3</sup> g <sup>-1</sup> STP)	317
Total Pore Volume <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	0.49
Micropore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	0.006

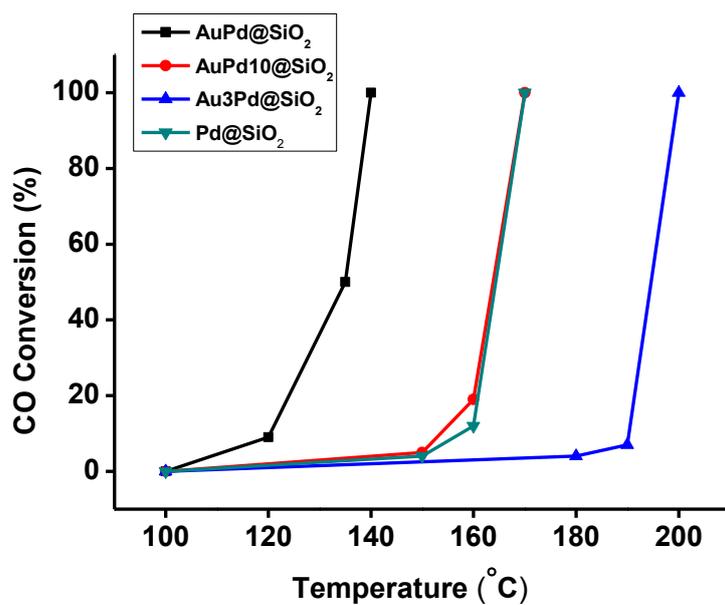
<sup>a</sup>Total pore volume measured at a relative pressure of P/P<sub>0</sub> = 0.99. <sup>b</sup> Calculated through t-plot analysis as a function of relative pressure using the Broekhoff de Boer model.



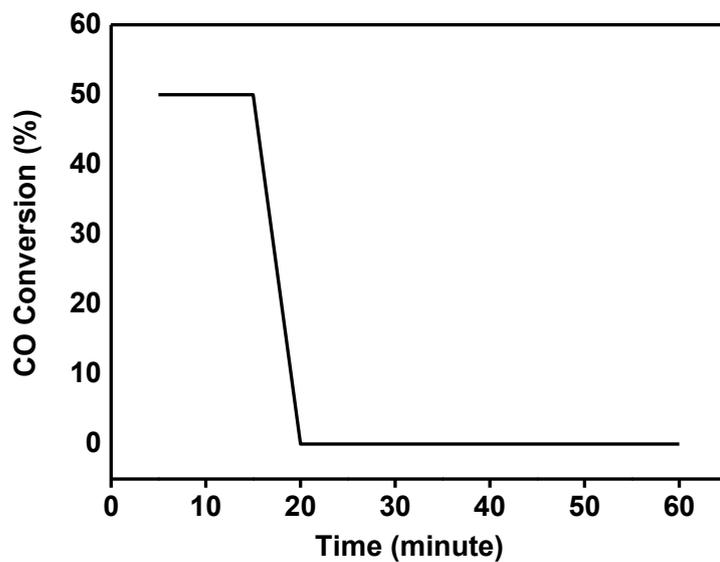
**Supporting Information Figure S14:** (top) N<sub>2</sub> adsorption – desorption isotherms of sample AuPd10@SiO<sub>2</sub> (bottom) Pore size distribution calculated from the adsorption branch of the isotherms by DFT method.

N <sub>2</sub> uptake (cm <sup>3</sup> g <sup>-1</sup> STP)	265
Total Pore Volume <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> ) <sup>a</sup>	0.41
Micropore Volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>b</sup>	0.04

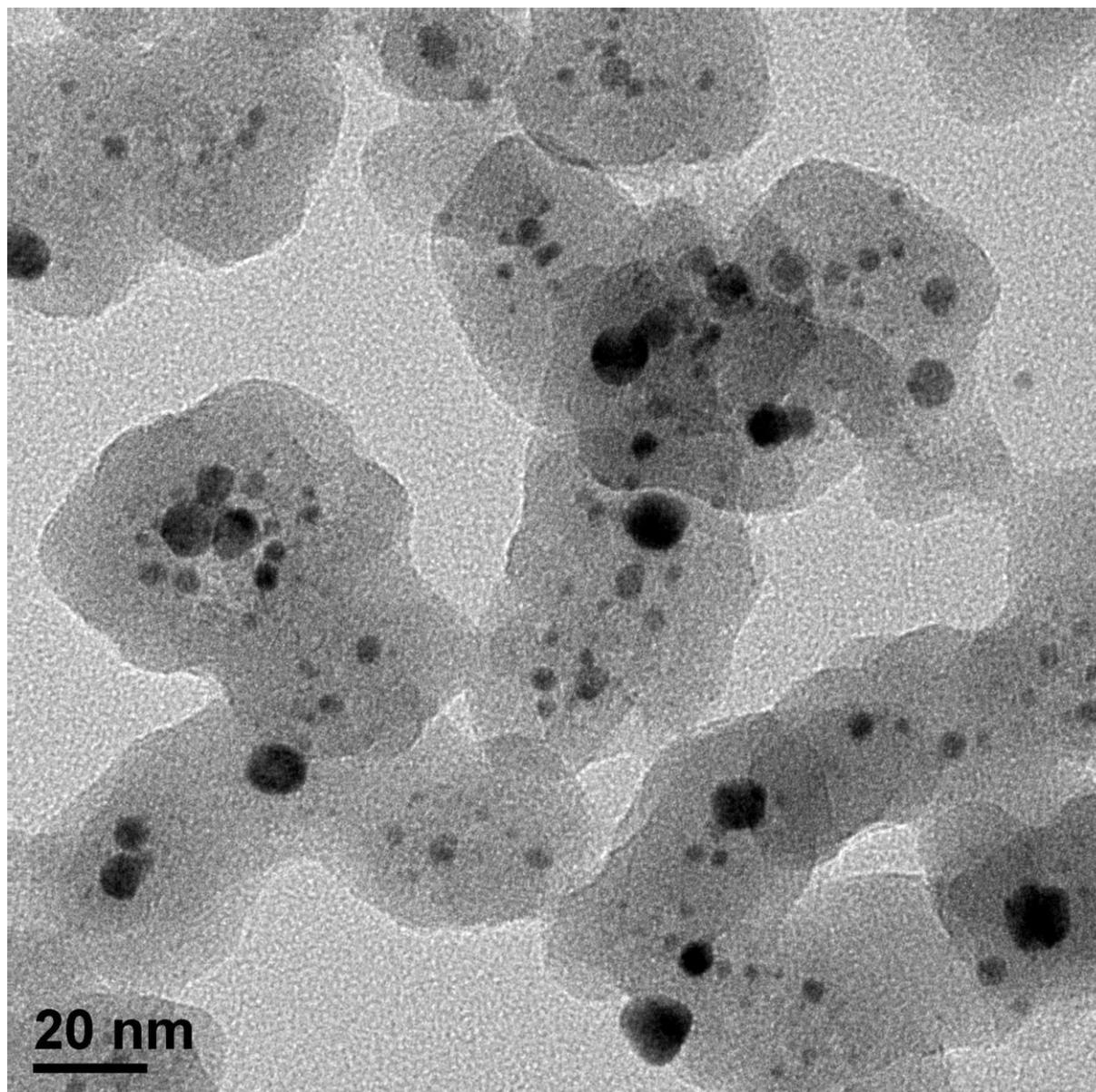
<sup>a</sup>Total pore volume measured at a relative pressure of P/P<sub>0</sub> = 0.99. <sup>b</sup> Calculated through t-plot analysis as a function of relative pressure using the Broekhoff de Boer model.



**Supporting Information Figure S15:** CO conversion with temperature by the four catalysts.

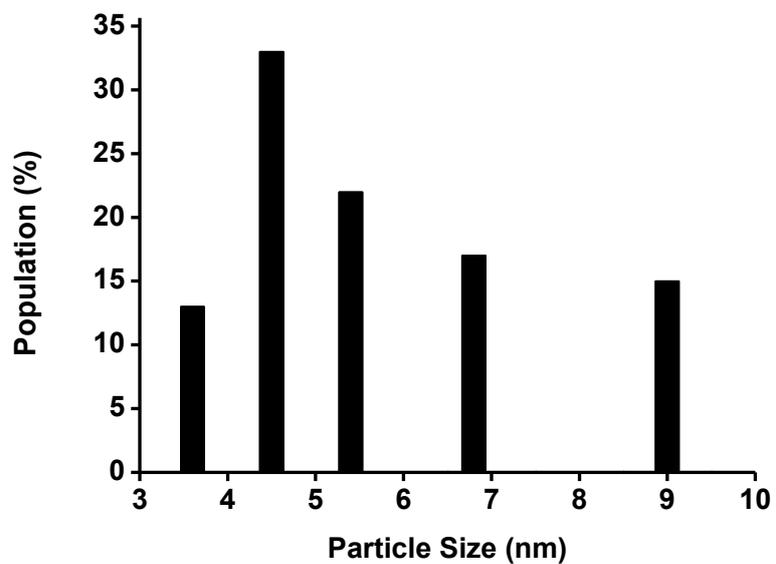


**Supporting Information Figure S16:** CO conversion as a function of time-on-stream by Au@SiO<sub>2</sub> at room temperature (28 °C).

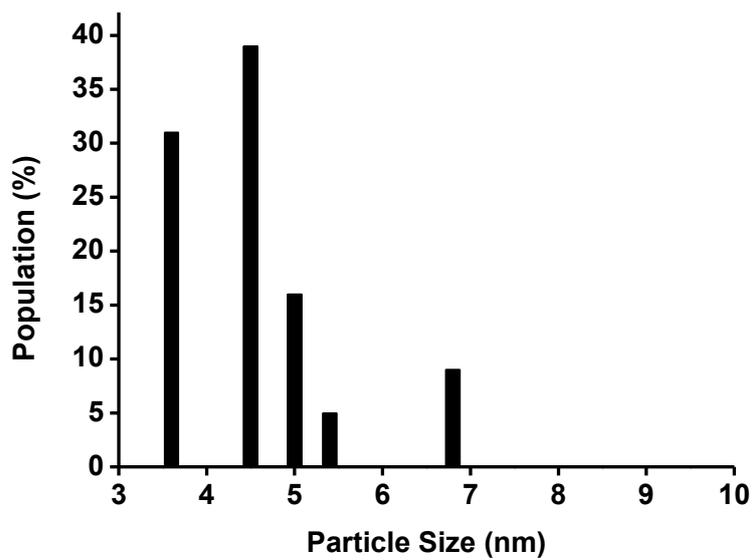


**Supporting Information Figure S17:** HRTEM image of Au@SiO<sub>2</sub> catalyst after CO oxidation study.

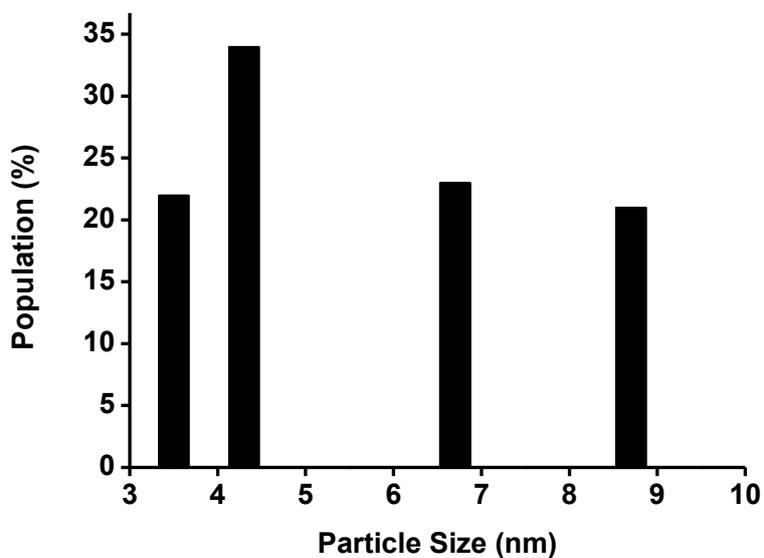
a)



b)



c)



**Supporting Information Figure S18:** Particle size distribution graph of a) Au<sub>3</sub>Pd@SiO<sub>2</sub>, b) AuPd@SiO<sub>2</sub> and c) AuPd<sub>10</sub>@SiO<sub>2</sub> catalysts calcined at 750 °C.

#### References:

1. A. Samanta, B. B. Dhar and R. N. Devi, *J. Phys. Chem. C*, 2012, **116**, 1748.
2. A. Samanta, B. B. Dhar and R. N. Devi, *ChemCatChem.*, 2013, **5**, 1911.